IN THE

Supreme Court of the United States

October Term, 1973

No. 73-1590

DYNEX INDUSTRIAL PLASTICS CORP.,

Petitioner,

v.

ANCHOR PLASTICS COMPANY, INC.,

Respondent.

PETITION FOR A WRIT OF CERTIORARI TO THE UNITED STATES COURT OF APPEALS FOR THE THIRD CIRCUIT

SUPPLEMENTAL APPENDIX

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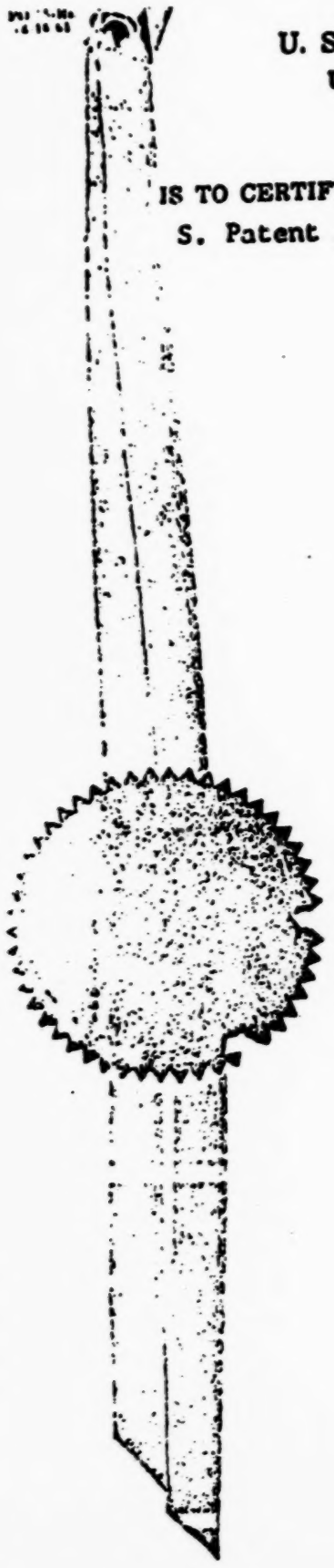
U. S. DEPARTMENT OF COMMERCE
UNITED STATES PATENT OFFICE

September 8, 1971
(Date)

IS TO CERTIFY that the annexed is a true copy from the records of this office
S. Patent 3,136,676.



PLAINTIFF'S EXHIBIT
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By authority of the
COMMISSIONER OF PATENTS

R. C. Sailer

Certifying Officer.

3,xxx,xxx

UNITED STATES PATENT OFFICE.

SEAL OF THE PATENT OFFICE.

Whereas ...ard A. Fisch, of Forest Hills Gardens, ... Wallis Hinkemeyer, and William ... executors of Richard A. Fisch, deceased, ... Products Company, Inc., of Long Island ... a corporation of New York,.

POOR COPY

PRESENTED TO THE COMMISSIONER OF PATENTS A PETITION PRAYING FOR THE GRANT OF LETTERS PATENT FOR AN ALLEGED NEW AND USEFUL INVENTION THE TITLE AND A DESCRIPTION OF WHICH ARE CONTAINED IN THE SPECIFICATION OF WHICH A COPY IS HEREUNTO ANNEXED AND MADE A PART HEREOF, AND COMPLIED WITH THE VARIOUS REQUIREMENTS OF LAW IN SUCH CASES MADE AND PROVIDED, AND

Whereas UPON DUE EXAMINATION MADE THE SAID CLAIMANTS are ADJUDGED TO BE JUSTLY ENTITLED TO A PATENT UNDER THE LAW.

NOW THEREFORE THESE Letters Patent ARE TO GRANT UNTO THE SAID

...al Products Company, Inc., ...s successors OR ASSIGNS

FOR THE TERM OF SEVENTEEN YEARS FROM THE DATE OF THIS GRANT

THE RIGHT TO EXCLUDE OTHERS FROM MAKING, USING OR SELLING THE SAID INVENTION THROUGHOUT THE UNITED STATES.

In testimony whereof I have hereunto set my hand and caused the seal of the Patent Office to be affixed at the City of Washington this ninth day of June, in the year of our Lord one thousand nine hundred and sixty-four, and of the Independence of the United States of America the one hundred and eighty-eighth.

(SEAL)

...Clarence Wilkes

...Commissioner of Patents

June 9, 1964 R. A. FISCH 3,136,676

METALLIZED PLASTIC EXTRUSION PRODUCTS AND METHOD OF MAKING SAME

Filed Feb. 20, 1957 2 Sheets-Sheet 1

FIG. 1.

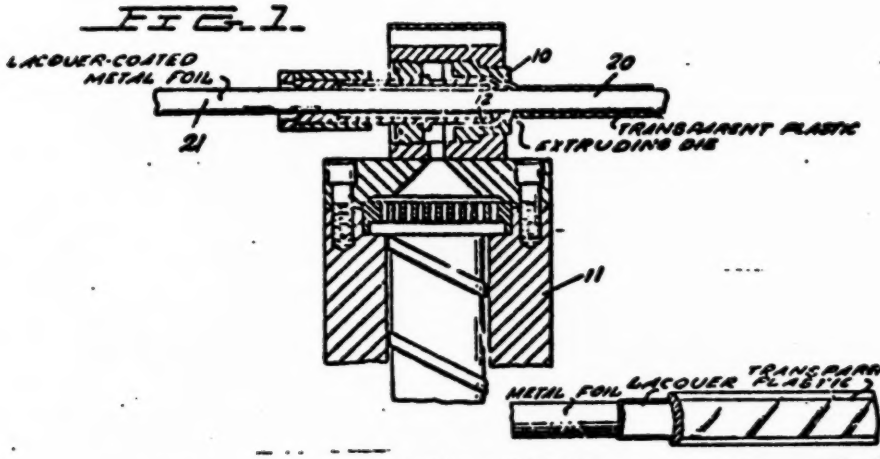

FIG. 1A.

FIG. 2.

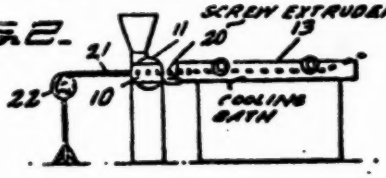

FIG. 3.

FIG. 4.

FIG. 5.

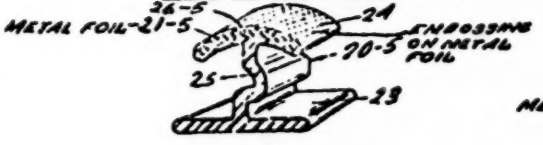

FIG. 6.

FIG. 7.

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Appendix F

June 9, 1964 R. A. FISCH 3,136,676

METALLIZED PLASTIC EXTRUSION PRODUCTS AND METHOD OF MAKING SAME

Filed Feb. 20, 1957 2 Sheets-Sheet 2

FIG. 10.

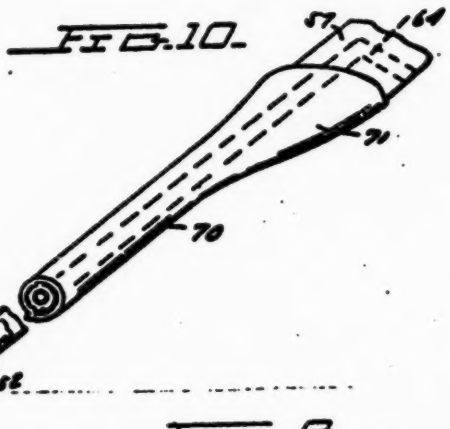


FIG. 8.

FIG. 9.

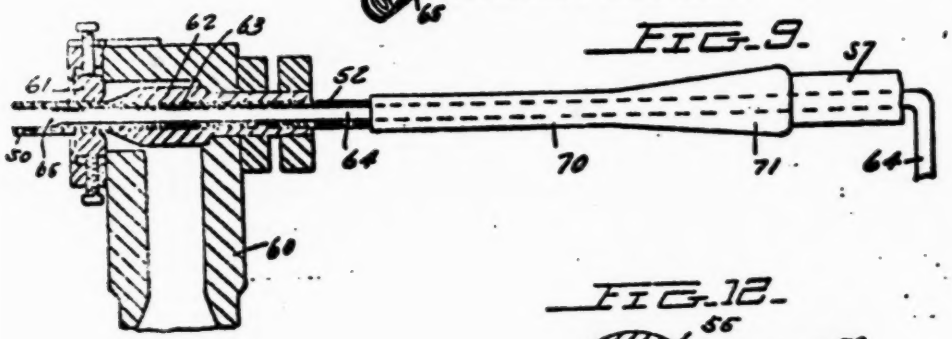


FIG. 12.

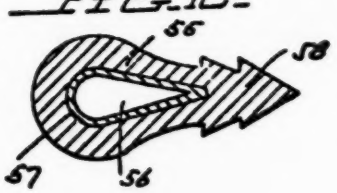


FIG. 11.

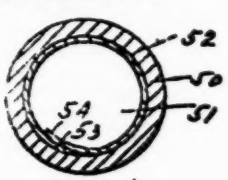
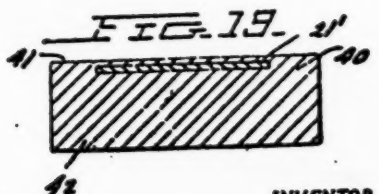


FIG. 19.



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Appendix F

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United States Patent Office

3,136,676

Patented June 9, 1964

1

3,136,676
METALLIZED PLASTIC EXTRUSION PRODUCTS AND METHOD OF MAKING SAME

Richard A. Fisch, Forest Hills Gardens, N.Y.; Hilde Fisch, Willie Schlossinger, and William Guggenheimer, executors of Richard A. Fisch, deceased, assignors to Anchor Plastics Company, Inc., Long Island City, N.Y., a corporation of New York

Filed Feb. 20, 1957, Ser. No. 641,358

5 Claims. (Cl. 156—244)

This invention relates to the production of metallized effects in extruded transparent thermoplastic products.

This application is a continuation-in-part of U.S. application Serial No. 497,948, filed March 30, 1955, now abandoned.

Processes of producing extruded thermoplastic materials with embedded reinforcing wires or strips are well known. Transparent or translucent plastic product which have a light-reflecting, metal-like region due to a thin coating of metal on an inside or outside surface are also known. When it was attempted to obtain a metal-like appearance in a plastic extruded product by embedding a metal foil therein, however, it was found that the inserted foil wrinkled so as to give the effect of an inferior product such as might be caused by distortion of the plastic or foil during extrusion or subsequent bending or flexing or by only loosely associating the foil with the plastic.

Among the objects of this invention is to provide a thermoplastic extrusion product with a light reflecting metallic effect in at least a portion thereof which metallic effect is not removed or injured by scratching or rubbing the surface of the plastic.

Among other objects of the invention is to provide an extrusion product comprising transparent thermoplastic material containing embedded therein, a thin, embossed, highly reflective metallic foil.

Among other objects of the invention is to provide a method of continuously embedding a metallic foil in transparent thermoplastic extrusion products of various cross sectional shapes so as to provide the product with a metallic effect and with an embedded foil which is substantially free from wrinkling and similar defects so that the foil appears as a smooth adherent layer in the interior of the plastic product.

It has heretofore been concluded that metallic foils were too distortable and of too delicate a nature to be embedded in plastics without distortion. Said prior application Serial No. 497,948 is based on the discovery that wrinkling of a thin metallic foil which is embedded in a thermoplastic during extrusion could be prevented by modifying the foil insert so as to permit one side thereof to move with the plastic more freely than the opposite side. It was found that in the ordinary process of extrusion with a delicate foil insert, some parts of the embedded foil adhered more to the thermoplastic layer on the front side thereof whereas other parts of the foil adhered more securely to the thermoplastic layer on the rear side thereof and when shrinkage or fleeting of the plastic occurred, wrinkles due to different tensions were formed in the foil. According to one modification of said prior application, this undesired effect is overcome by embedding a laminated foil having two or more layers so that one layer of the foil can slip with respect to the other layer of foil while the outside surface of the foil adheres to the plastic. According to a second modification the undesirable wrinkling is overcome by applying an adhesive layer to one side of the foil to be embedded.

It has now been found that it is possible to apply a thermoplastic adhesive to one or both sides of the foil to be embedded so that the said one or both sides of the foil are very securely adhered to the plastic material and

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will not wrinkle during or after the extrusion even when the extruded product is severely distorted.

One difficulty connected with securing adhesion between the foil and the plastic is that the foil as it is received contains a very thin layer of oil or lubricant which has been applied during the manufacture thereof. Foils which have been treated to remove the lubricant can be ordered but even such foils contain a residual amount of the lubricant. If the adhesive which is applied to the foil is to be very effective, it must be one which is capable of absorbing or overcoming the non-adhesive effects of the lubricant film. Very satisfactory adhesives which act as adhesives between the foil and plastic in spite of the residual lubricant or oil on the foil are lacquers with a nitrocellulose base. Cellulose butyrate lacquers and vinyl acetate-vinyl chloride copolymer lacquers are also satisfactory.

The extruded product may be of any configuration. Where the products are tubular or hollow, the entire inside of the tubular or hollow portion may be lined with the adherent foil. Thus, even though the metallic portion is only a foil, such tubular products act effectively as electromagnetic shields in electronic devices. Where both sides of the foil are adhesively coated the edges of a foil inside a tube of plastic will be united to produce a fluid-tight metal conduit.

An additional effect is obtained when embossed foils are employed in the process. The foils may be embossed so as to emphasize the light reflecting properties (i.e., so that light is reflected in a multiplicity of directions), and/or to improve the flexibility of the foil. Such products are especially useful as highway markers. The transparent plastic may be colored, red, green, or similar colors so that the light reflected therefrom, is similarly colored. The embossed designs on said foil does not interfere with the extruding process of the invention.

The invention is especially adapted for the production of decorative mouldings, beads and trim strips for cabinets, walls and frames, panel joining strips, decorative designation strips, highway and similar danger markers, etc.

The invention both as to its organization and its method of operation together with additional objects and advantages thereof will best be understood from the following description of specific embodiments thereof when read in connection with the accompanying drawing in which

FIG. 1 is a cross-sectional view of the end of a cross head type of extrusion device as it is applied to the process of the present invention.

FIGURE 1A is a partial sectional view of the article emerging from the process disclosed in FIGURE 1.

FIG. 2 is a front view of an apparatus used to carry out the process of the present invention.

FIGS. 3, 4, 5 and 6 are cross-sectional perspective views of various forms of extrusion products made according to one form of the invention.

FIG. 7 is an enlarged cross sectional view of a portion of an extrusion product made according to the invention.

FIG. 8 is a cross sectional view of another extrusion product made according to the invention.

FIG. 9 is a cross sectional view of an extruding device extruding a tube while lining the same with a metal foil.

FIG. 10 is a detail view, partially broken away, of the means for curving the foil in the extruding device of FIG. 9.

FIG. 11 is a cross sectional view of a product made by the process and apparatus of FIG. 9.

FIG. 12 is a cross sectional view of another product such as made by the process and apparatus of FIG. 9.

FIG. 13 is a cross sectional view of a modified form of product made according to the invention.

A typical cross head type of plastic extrusion apparatus is shown in FIG. 1. In such an apparatus the direction of movement of the extruded product 20 from the extrusion die 10 is at an angle (in this case 90°) to the direction of movement of the plastic material through the screw extrusion device 11.

Such a crosshead extrusion apparatus is advantageous for extruding any type of thermoplastic product containing an embedded material since the material being embedded 21 does not have to pass all the way through the screw extruder 11 and does not have to be bent in order to get to the interior of the extrusion die 10. The die 10 comprises the core 12 through which the embedding material 21 is adapted to pass. This type of extrusion apparatus itself is known and is not a part of the present invention so that details of the apparatus are not described. As an illustration, however, the embedding foil 21 is held in the form of a roll 22 and is continuously fed to the cross head die 10 of the screw extruder 11. After passing through the die, the extruded product 20 is passed through a cooling bath 13.

Depending on the shape of the die, etc., various shapes and effects may be produced by the process as illustrated in FIGS. 3–6. FIG. 3 shows a U-shaped product 20–3 of cellulose acetate containing a layer of foil 21–3 which is coated on the top surface with a layer 26 of cellulose nitrate lacquer which extends beneath substantially all of the outside surface regions of the product.

FIG. 4 shows an angle moulding 20–4 with a layer of foil 21–4 which is coated with a layer 26–4 of cellulose nitrate lacquer, extending beneath substantially the entire surface regions of the product. In these figures the thickness of the layer of cellulose nitrate lacquer is exaggerated for the sake of clarity. In the product this layer may actually disappear and blend in with the cellulose acetate of the main body of the product.

FIG. 5 shows a moulding 20–5 having a rear planar section 23, a front planar section 24 connected by the section 25. In this product only the front section 24 contains the foil 21–5 beneath its surface. The foil 21–5 is coated with a thin layer of adhesive lacquer 26–5 which may have a base of cellulose butyrate, cellulose nitrate, ethyl cellulose, polyvinyl acetate-polyvinyl chloride.

As illustrated in FIGS. 3, 5 and 6 the foil 21–3 may be embossed. An especially useful product is obtained where the foil contains a multiplicity of minute ovate or faceted projections or depressions so as to reflect light in a multiplicity of directions.

In the product 20–6 of FIG. 6 two spaced portions thereof contain the embedded foils 21–6 containing layer 26–6 of plastic adhesive.

In FIG. 7, the product 20–7 contains a single layer of foil 121. On the front surface of the foil 121 is a layer of plastic 122 which is compatible with the plastic 123 of the product. The plastic 122 blends with the hot plastic 123 during the extrusion process and since previously to the extrusion, the foil 121 has been coated with plastic 122 so that a good and uniform adherence is obtained, the foil 121 is effectively united to the product 20–7.

In addition, or in place of the layer 122 of FIG. 7, the lubricating layer 124 of silicone resin may be applied to the rear side of the foil 121.

The width of the foil employed in the process may be from about ⅛ of an inch in FIG. 6, for example, up to six inches or more. In the specification and claims the term laminated foils will be understood to include folded foils as well as coated foils.

FIG. 8 shows in cross section, an extruded strip 20–8 containing the embedded foil 21–8 to the top surface of which (and also, if desired, to the bottom surface) a lacquer adhesive has been applied. The top surface of the plastic body 29 contains a plurality of longitudinal flutes 30, 31 and the spaces 32, 33, 34 flanking the flutes have been partially filled with paint or a pigment material.

The foil employed for such products may be any type of foil but aluminum foil is very satisfactory being easily available and having high reflectivity. The color or appearance of the product may be changed by coloring the transparent plastic material. Thus, a gold bronze or brass appearance may be obtained by coloring the plastic different shades of yellow. An unusual effect is obtained in the product 40 of FIG. 13 wherein the foil 21' is inserted close to one surface 1 of the product. When the plastic of 40 is colored a light yellow the insert 21' as seen from the surface 41 has a silvery appearance whereas the same foil 21' as seen from the surface 42 had a gold appearance.

The bodies 50 and 55 of FIGS. 11 and 12, respectively, have a hollow portion 51 or 56 therein which is lined with a metal foil 52 or 57. Each of these foils is treated on at least the one side which contacts the plastic with an adhesive lacquer solution which is not shown in the drawing. Such products may be made by the process and apparatus illustrated in FIGS. 9 and 10. In this apparatus the plastic material to be extruded is forced through cylinder 60 to die 61 which has an internal core portion 62 for forming the hollow part of the extruded product. A straight opening 63 extends through the core 62 from the die 61 to the side opposite the die 61. The foil tube 52 is fed through this opening 63. Extending through the opening 63 of core 62 is also a tube 64. This tube prevents the foil tube 52 from collapsing and admits air to the interior of the formed tube through the flared opening 65 at the end thereof. The flared end also acts to press the foil tube 52 against the inside surface of the hot extruded plastic tube to assure a union between the thermoplastic adhesive on the surface of the foil and the body of the plastic tube.

The foil tube 52 is automatically formed from a strip of film 57 by passing through the tube forming device 70 having a funnel shaped end 71 adjacent the entrance end of the foil strip 57.

Where both sides of the foil 52 have been coated with an adhesive thermoplastic lacquer, the heat and pressure applied to the foil as it passes between the flared end 65 of the tube 64 and the extruded plastic tube 50 also seals the overlapping edges 53, 54 of the foil.

The hollow strip 55 shown in cross section in FIG. 12 has a notched edge 58 adapted to be forced into a groove to provide a beaded decoration.

The following example further illustrates the process of the invention.

Example 1

A foil which is embossed so as to reflect light at a multiplicity of angles is sprayed on one side with a solution of cellulose nitrate lacquer. The thickness of the layer of cellulose nitrate deposited thereon may be about .001% or less, for example. This foil is fed to an extrusion apparatus such as shown in FIG. 1 with the coated surface facing in such a direction as to be adjacent the front surface of the product to be extruded. A reflective extruded strip without wrinkles or distortions in the embedded foil is obtained. When the plastic is dyed red prior to extrusion a bright red reflection is obtained in the finished product when a light is cast upon the product.

The surface of the foil may be scratched to produce a burnished effect in the finished product. A satin effect may be obtained by brushing or frosting the surface of the plastic. Various combinations of foil treatment and plastic surface treatments may be applied.

The adhesive may be applied to the front surface and to the rear surface of the foil.

The features and principles underlying the invention described above in connection with specific exemplifications will suggest to those skilled in the art many other

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modifications thereof. It is accordingly desired that the appended claims shall not be limited to any specific feature or details thereof.

I claim:

1. In the process of preparing extruded thermoplastic products with at least one visible region thereof having a metallic appearance, the steps comprising

providing a metal foil having a thin, film-like coating of a transparent thermoplastic lacquer of the group consisting of cellulose nitrate, cellulose butyrate, ethyl cellulose, and polyvinyl acetate-polyvinyl chloride lacquers on at least one surface thereof,

extruding a transparent thermoplastic material about the lacquer-coated foil while feeding the foil in unison with the thermoplastic material with the surface of the foil containing the lacquer coating contacting the interior surface of the extruded material whereby the lacquer-coating of the foil adhesively fixes the position of the latter with respect to the extruded material.

2. The process as set forth in claim 1 in which the metal foil is an embossed foil containing a multiplicity of facets adapted to reflect light in various directions.

3. The process as set forth in claim 1 in which the metal foil comprises a layer of said thermoplastic lacquer on the surfaces of both sides thereof and in which the thermoplastic material is extruded to contact both lacquer-coated sides of said film.

4. In the process of preparing extruded thermoplastic products with at least one visible region thereof having a metallic appearance, the steps comprising

providing a metal foil having a thin, film-like coating of transparent cellulose nitrate lacquer on at least one surface thereof,

extruding a transparent thermoplastic material about the lacquer-coated foil while feeding the foil in unison with the thermoplastic material with the surface of the foil containing the lacquer coating contacting the interior surface of the extruded material whereby the lacquer-coating of the foil adhesively fixes the position of the latter with respect to the extruded material.

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5. In the process of preparing extruded thermoplastic products with at least one visible region thereof having a metallic appearance, the steps comprising

providing a metal foil having a thin, film-like coating of transparent cellulosic lacquer on at least one surface thereof,

extruding a transparent thermoplastic material about the lacquer-coated foil while feeding the foil in unison with the thermoplastic material with the surface of the foil containing the lacquer coating contacting the interior surface of the extruded material whereby the lacquer-coating of the foil adhesively fixes the position of the latter with respect to the extruded material.

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Appendix G

EXHIBIT Q -U.S. PATENT 2,774,811 - A. SHANOK ET AL E1

Dec. 18, 1956 A. SHANOK ET AL 2,774,811

ANTENNA AND TRIM

Filed March 2, 1954

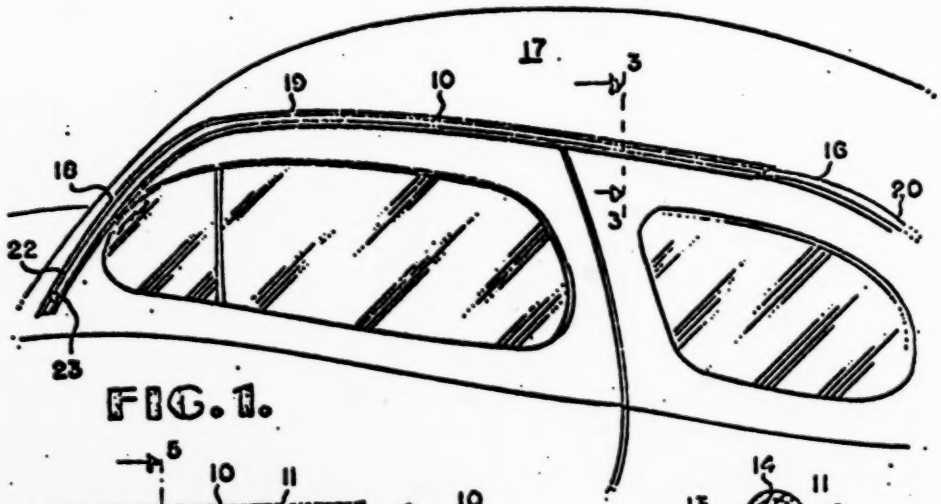

FIG. 1.
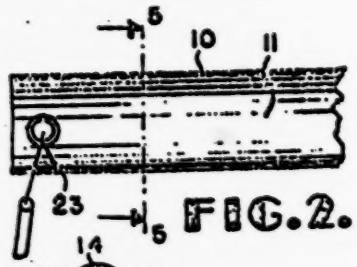
FIG. 2.

FIG. 3.

FIG. 5.

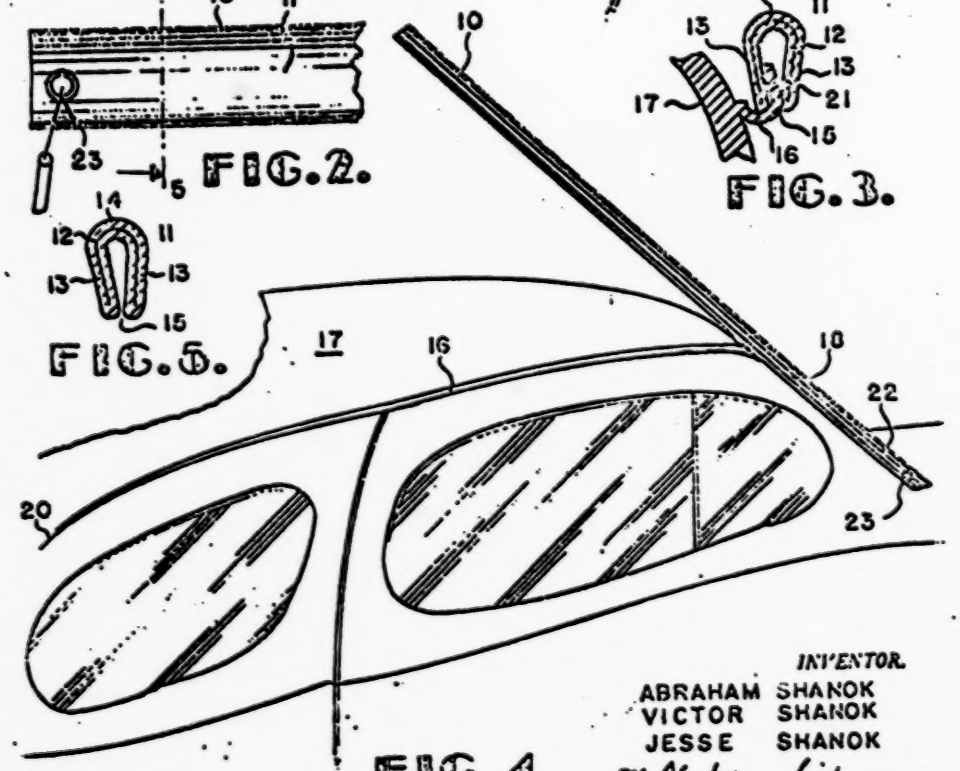

FIG. 4.

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United States Patent Office 2,774,811 Patented Dec. 18, 1956

2,774,811

ANTENNA AND TRIM

Abraham Shanok, Victor Shanok, and Jesse Shanok, Brooklyn, N. Y.

Application March 2, 1954, Serial No. 413,524

2 Claims. (Cl. 174—110)

This invention relates to a radio antenna and decorative trim particularly adapted for use on motor vehicles.

It is one of the objects of this invention to provide an antenna for motor vehicles which is capable of simultaneously functioning as a decorative trim for such vehicles and which may be readily mounted thereon without the use of any special tools and which when so mounted will be maintained in operative position in a firm and secure manner without the use of any special fastening means.

It is a further object of this invention to provide a device of the character indicated which is capable of being applied to a motor vehicle or similar object or any other device having a relatively thin lip, edge or flange and conforming itself to the contours of the ledge or flange to which it is applied and along which it extends.

Another object of this invention is to provide a device of the character indicated which is capable of being readily applied to a motor vehicle along any projecting lip, edge or flange and which when so applied will blend pleasingly with the decorative scheme of the vehicle and add to the aesthetic appearance thereof.

It is also an object of this invention to provide a decorative device of the character indicated which is capable of being formed in strips of substantial length so that any desired length thereof may be readily applied to a motor vehicle.

This invention has for a further object the provision of an antenna in strip form which is capable of being readily mounted upon a metallic object such as the body of a motor vehicle and which is capable of functioning for the purpose of the reception of radio waves in an efficient and effective manner.

It is also an object of this invention to provide a strip of the character indicated which may be readily and efficiently manufactured on a large scale at relatively low cost.

Other and further objects, benefits and advantages of this invention will become apparent from the description thereof contained in the annexed drawings, specifications and claims or will otherwise become obvious. It will be understood that the invention herein disclosed may be employed for other purposes for which the parts, structure and arrangement are adapted.

In the accompanying drawings:

Figure 1 is a perspective view of a portion of a motor vehicle showing the instant invention applied thereto along the rain gutter or drip guard portion thereof,

Figure 2 is a fragmentary side elevational view of a portion of the antenna and trim strip comprising the instant invention,

Figure 3 is a cross-section of Figure 1 taken along line 3—3 thereof,

Figure 4 illustrates the antenna and trim as applied to the forward portion of the rain gutter of a motor vehicle to form a substantially vertically extending antenna, and

Figure 5 is a cross-section of Figure 2 taken along line 5—5 thereof.

As shown in the accompanying drawings, particularly Figures 2, 3 and 5, the device is comprised of an elongated channel strip designated generally by the numeral 10. Strip 10 is of substantially U-shaped cross-section. The strip is formed of a synthetic resin or plastic material which is relatively rigid but capable of being flexed sufficiently to conform to the contours of an object to which it is applied and along which it extends as will more clearly appear hereafter.

Encased within the plastic or synthetic resin material forming the body 11 of the strip and completely enveloped thereby is a tape or ribbon of conductive material such as metal foil 12. It is preferred to form strip 10 by extending the plastic insulating material over the tape or ribbon of metal foil 12. The foil is thereby encapsulated within the plastic insulating body 11. In practice it has been found advantageous to utilize a transparent plastic material which is extruded over a ribbon of aluminum foil to thereby form a continuous strip which closely resembles the chrome or stainless steel stripping or decorative trim material which is customarily applied to the body of a motor vehicle. A suitable plastic material for this purpose is cellulose acetate butyrate although it will be understood that other similarly suitable plastic materials may be employed for this purpose.

Said channel strip being substantially U-shaped is thus comprised of a pair of opposed arms or sides 13 and a closed end or bight portion 14 connecting said sides. The end or bight portion 14 which connects the sides of said U-shaped body is substantially semi-circular in cross-section and said sides 13 converge toward each other along their free ends. The free ends of the side portions of the channel body are positioned close together and in substantial contiguity along the length of the channel strip body thereby forming a very restricted longitudinally extending opening therefor as shown at 15.

The strip may be mounted along any comparatively thin projection such as a rim, ledge or flange which is customarily formed on various portions of an automobile body. Thus for example it may be applied along the lip or free edge of the drip guard or rain gutter usually surrounding the door frame openings and extending along the top of a vehicle; the marginal lip or rim of the doors thereof or the flange or rim usually surrounding the cover of the trunk compartment. The strip 10 is applied along any such thin projection by inserting said lip or projection into the longitudinally extending opening 15 between the free ends of the side arms 13. The open portion of the strip body is applied against the projection and the channel strip is then pressed thereon along the length of the projection. The pressure thus applied spreads the free ends of the side arms and thus permit the projection to enter the channel portion of the strip. The side arms 13 are thus sprung apart a sufficient distance to receive the projection; the plastic material being sufficiently resilient for this purpose. The strip may be readily pressed onto the projection progressively along the length thereof. When the strip has thus been mounted upon a lip or projection of this character the resilience of the arms causes them to tend to return to their normal initial position and bear against said projecting body or lip to thus firmly mount and maintain the strip in position thereon. As has been heretofore indicated, the strip is capable of being bent or flexed along its longitudinal axis so that it may be mounted along a projection having a longitudinal curvature formed therein and when so mounted will conform to such curvature thereof.

It should be noted that the metallic strip is entirely enveloped by the insulating plastic material and is thus spaced and insulated from the metallic body of the projection. Furthermore, in view of the tapered cross-section of the strip due to the converging relation of the arms 13,

the projection or lip upon which the strip is mounted is gripped principally in the region of the free ends of the arms, the upper portions of said arms as well as the semi-circular end or bight portion being spaced substantially from the metal lip projection. Thus the foil is spaced from the metal body of the vehicle by the interposition of the plastic dielectric material of the strip along the side edges thereof, the main body of the foil being spaced therefrom much more substantially and with the added interposition of the dielectric effect of the air therebetween. As a result of this arrangement the capacity effect which may exist between the conductive ribbon foil and the metallic body of the vehicle is substantially reduced thereby materially increasing the efficiency of the antenna strip in the interception of radio waves. Connection of the antenna to the conventional lead-in cable leading to the antenna input terminal of the radio receiver is readily accomplished by means of an electro-conductive metallic connector such as a rivet 23 attached to the foil through an opening 16 in the insulating material, said rivet being electrically connected to the antenna lead-in cable.

The manner in which the antenna and trim strip 10 is applied to the drip guard or rain gutter 16 of a motor vehicle is more particularly illustrated in Figures 1 and 3. The drip guard 16 is comprised of an open channel secured to the body 17 of the motor vehicle and usually extends substantially vertically forward of the upper portion of the car door frame as shown at 18, thence along the top of the vehicle along the door frames as shown at 19 and around the upper portion of the rear door frame as shown at 20. Strip 10 is mounted upon the drip guard 16 by forcing the lip 21 of the drip guard between the opening 15 of the free ends of the sides 13 of the strip. The sides 13 of the strip are thus forced or sprung apart and the lip 21 is resiliently gripped between the end portions of said side arms.

One end 22 of strip 10 is provided with a suitable lead-in cable connector as shown at 23. The strip is advantageously applied by pressing it upon the lip 21 of the drip guard 16 beginning with end 22 and then progressively pressing the remainder of the strip along said guard. In this manner the lip will progressively enter the opening 15 extending longitudinally of strip 10. As the strip is applied it automatically flexes longitudinally to accommodate itself to the curvature of the bend formed as the substantially vertical forward portion 18 of the guard merges with portion 19 of the guard extending horizontally along the top of the vehicle. The antenna may be applied in any length desired. In view of the transparency of the plastic the visible aluminum foil presents an appearance which blends pleasingly with the general chrome and metal trim on the vehicle and is completely unobtrusive. When applied to this particular portion of the car it presents no unsightly projection and is substantially unrecognizable and indistinguishable. If desired, a similar strip may be applied along the other side of the automobile and said antenna strips may be independently connected to radio apparatus within the car or they may be interconnected for the purpose of improving reception in a manner well known to those skilled in the art. Said additional strip may also be left unconnected and thus utilized to produce a balanced decorative appearance for the motor vehicle. Thus the strip may be utilized as a decorative element substantially enhancing the appearance of the car.

Figure 4 illustrates another manner in which the strip may be applied to a motor vehicle body to serve the purpose of a substantially vertical antenna. In this form of application of the invention the strip 10 is mounted along

the forward portion 18 of the gutter or drip guard 16 only. The strip is used in sufficient length to extend upwardly beyond the top of the automobile to the extent desired. The resilient grip of the sides 13 of the strip against the portion of the lip 21 of the gutter along which it extends is sufficient to support the freely extending portion of the antenna. The antenna is connected to the lead-in cable of the car radio by means of a connecting element as shown at 23 in the manner heretofore described. It will be understood that the antenna and decorative trim comprising the present invention may be mounted upon or applied to other portions of a motor vehicle having a suitable projecting portion or to other structures or devices upon which it is adapted to be mounted by reason of the arrangement thereof.

We have here shown and described a preferred embodiment of our invention. It will be apparent, however, that this invention is not limited to this embodiment, and that many changes, additions and modifications can be made in connection therewith without departing from the spirit and scope of the invention as herein disclosed and hereafter claimed.

Having disclosed our invention, what we claim as new and desire to secure by Letters Patent is:

1. A radio antenna for a motor vehicle including a relatively thin projecting lip member comprising an elongated channel-shaped body portion of substantially U-shaped cross-section, said body portion including opposed sides and an enclosed end and being formed of an electrically insulating synthetic resin, a metal foil ribbon extending longitudinally through said strip and enveloped thereby, said enclosed end being substantially semi-circular in cross-section, said opposed sides converging toward each other along their free ends, said free ends being positioned in substantial contiguity to form a longitudinally extending opening for said body whereby said projecting lip is adapted to be received between said opposed sides and to be resiliently gripped therebetween and means for electrically connecting said metal foil to the input terminal of radio equipment within said vehicle.

2. A radio antenna for a motor vehicle including a relatively thin projecting lip member comprising an elongated channel-shaped body portion of substantially U-shaped cross-section, said body portion including opposed sides and an enclosed end and being formed of an electrically insulating synthetic resin, a metal foil ribbon extending longitudinally through said strip and enveloped thereby, said enclosed end being substantially semi-circular in cross-section, said opposed sides converging toward each other along their free ends, said free ends being positioned in substantial contiguity to form a longitudinally extending opening for said body whereby said projecting lip is adapted to be received between said opposed sides and to be resiliently gripped therebetween, said semi-circular end portion being spaced from said projecting lip and means for electrically connecting said metal foil to the input terminal of radio equipment within said vehicle.

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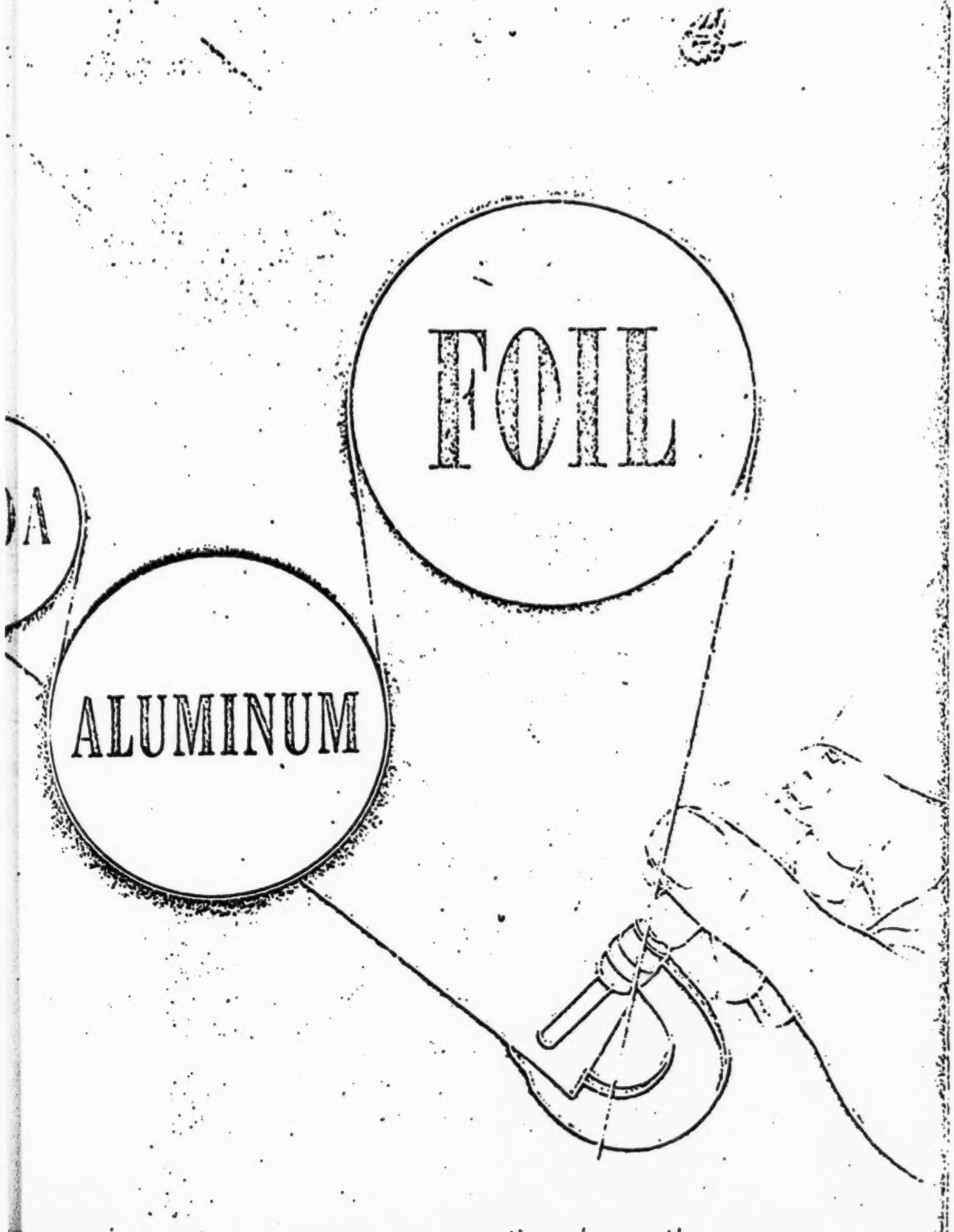
EXHIBIT X - EXCERPTS -"ALCOA ALUMINUM FOIL" - 1953 E4



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LCOA

LUMINUM

)IL

e properties

nd uses

ALUMINUM COMPANY OF AMERICA was the first commercial producer of aluminum foil in the United States. Today, as a result of Alcoa's early pioneering before World War I, aluminum foil is the most available, most economical and most commonly used metal foil. The spectacular increase in the use of aluminum foil parallels the rapid expansion of the aluminum industry, which is supplying this versatile, lightweight metal for thousands of old and new uses in numerous fields of application. This booklet contains general technical information about Alcoa aluminum foil which will aid those responsible for the selection and use of the proper material.

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holes seem to be an inevitable result of rolling tal to very thin gages. The best rolling practices d equipment seem able only to control the size d number.

From measurements under the microscope, the al area of all the pinholes in 100 square inches of 004 inch foil was estimated to be about 0.00004 uare inch. This value is almost insignificant. It is imated that a single hole of this area would rmit water vapor transfer at a rate of about .19 ams per twenty-four hours per 100 square inches th air at 100 per cent relative humidity and 0° F.

Table 3

TYPICAL VARIATION OF PINHOLES WITH GAGE

100 sheets of foil, 12" square, were examined for each gage.

Gage of foil in inches	Number of sheets with pinholes	Number of sheets with no pinholes
0.00035	100	None
0.0005	100	None
0.0007	15	85
0.001	8	92

The permeability or protective characteristics of different specimens of foils may be illustrated by their resistance to water vapor transmission. See Table 4.

WATER VAPOR TRANSFER

An indication of the effect of pinholes upon water vapor transfer is given by data in Tables 3 and 4, which present characteristic water vapor transfer values for foil of four different gages commercially used in packaging. In making this test, 100 sheets (12 inches square) of each gage of foil were taken and every tenth sheet tested for water vapor transfer. In the case of .001 inch foil, however, only eight of the one hundred sheets showed pinholes in the test and in the case of .0007 inch foil, only fifteen of the one hundred sheets showed pinholes. In the heavier gages, only

Table 4

WATER VAPOR TRANSMISSION OF THIN ALUMINUM FOILS*

Thickness of foil in inches	W.V.T. (gram water per 100 sq in. per 24 hours with air at 100°F and 100% R.H.
0.00035	0.62
	0.11
	0.20
	0.23
	0.15
	0.69
	0.29
	0.34
	0.18
	0.07
Average	0.29
0.0005	0.08
	0.05
	0.06
	0.12
	0.15
	0.09
	0.13
	0.31
	0.17
	0.04
Average	0.12
0.0007	0.07†
	0.08
	0.06
	0.05
	0.04
	0.08
	0.01
	0.04
0.001	0.02†
	0.03
	0.02

*Water vapor transmission determined by General Foods' Southwick method. Every tenth sheet of the 100 specimens of each gage inspected for pinholes (Table 3) was selected for water vapor transmission tests.

†Water vapor transmission values not averaged because majority of 100 sheets examined had zero permeability.

foil converting operations

The inherent functional and decorative characteristics of aluminum foil can be utilized and enhanced by converting operations to meet hundreds of applications. Conversion of aluminum foil comprises the following general operations:

1. Lacquering or coating
2. Laminating
3. Printing
4. Embossing
5. Shearing

Details of equipment for the various foil converting operations vary from one type unit to another and are outside the scope of this booklet. However, some desirable and necessary features will be given that are generally applicable in one form or another to the equipment used in converting foil.

TENSION CONTROL

In converting operations, special attention should be given to the proper handling of the foil. Controlled tension is essential to smooth unwinding and rewinding of the coiled stock. It assists in maintaining an unwound section of foil flat and free from wrinkles during converting operations. Adequate power facilities for braking and driving the machine are essential in providing a satisfactory tension. A constant tension, regardless of coil diameter, controlled to function automatically with uniform acceleration or instant deceleration of the drive, is desirable at all times and essential to high speed operations. Applied tension should not exceed the yield strength of the web, and a safe tension value is normally about one-half of the ultimate tensile strength. In the case of annealed foil, this is three pounds per inch of width per mil of thickness. For hard metal it is seven or eight pounds per inch of width per mil of thickness. To avoid breaking or strain hardening, annealed foils should not be subjected to any greater tension than is necessary to promote and maintain a smooth web.

SUPPORT AND IDLER ROLLS

Handling equipment should be so designed as to minimize all distances over which the foil is unsupported. This can be accomplished by the use of supports of well-balanced idler rolls having good bearings and smooth surfaces. Proper arrangement of guide rolls to alter the direction of travel for the foil web or to form compression contacts (nip rolls) assists in maintaining flatness and tension. Proper arrangement is particularly advantageous in preparing the foil web for contact with coating roll.

A good device for supporting the foil and removing wrinkles and fullness in the metal is a spreader or herringbone roll, as illustrated in Fig. 2. The herringbone roll is a helically grooved roll, which may be from 4 inches to 12 inches in diameter. Foil is threaded over the herringbone roll with a wrap of 30 per cent, depending on the gage and condition of the foil, so that the metal spreads outward to prevent the formation of wrinkles and creases.

Several types of conveyors may be used satisfactorily in drying ovens of finishing machines to support the foil web between the application unit and the rewind stand. Slat type conveyors or rod type conveyors, as well as idler rolls placed 12 inches to 18 inches apart, are frequently used.

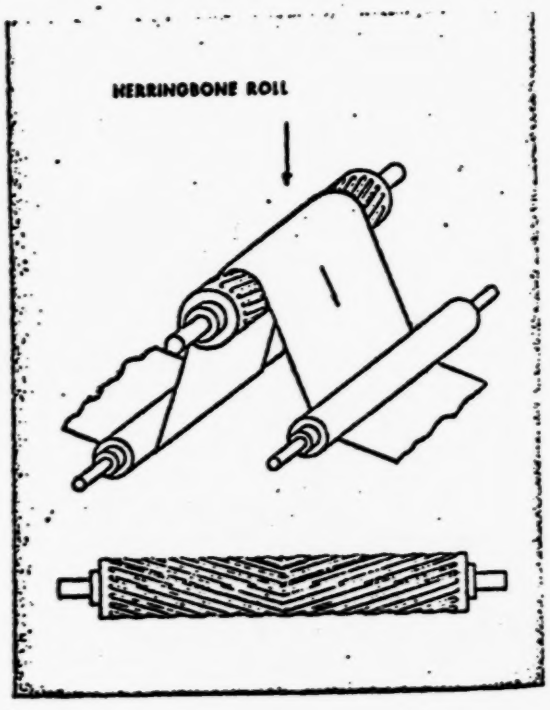
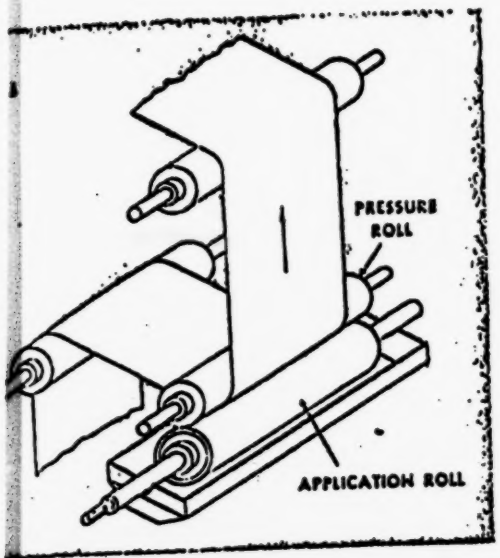


Figure 2. **HERRINGBONE IDLER ROLL**
Passing the material web over a herringbone idler roll will assist in reducing the apparent wrinkles coming from an irregular web.

application methods



...3. SQUEEGEE APPLICATION UNIT

...pplying unit, the bottom or application roll of soft rubber ...ially submerged in the coating medium. Rotating with the ...at a speed slightly less than the web velocity, the application ...ries the coating on to the web at the contact point between ...plication roll and top pressure roll.

...metal pressure roll is adjustable in relation to the applica... roll. By varying the pressure, squeegee action will regulate ...mount of coating applied to the web.

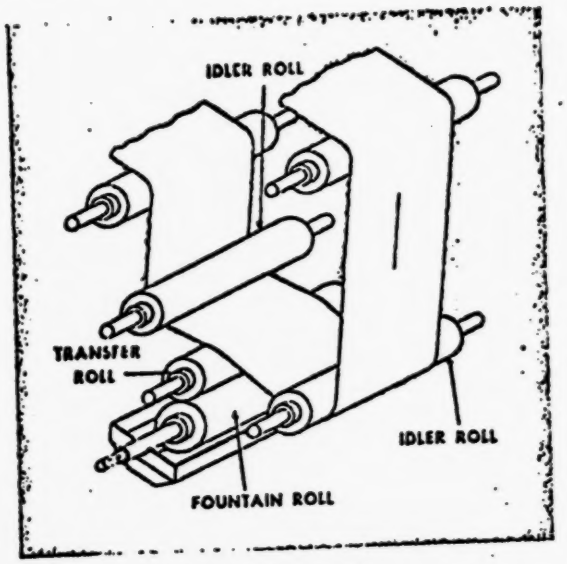
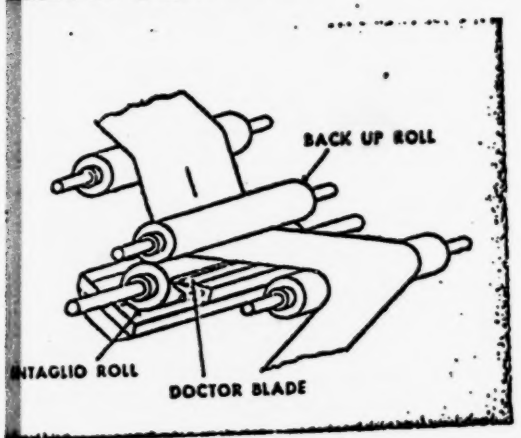


Figure 4. TRANSFER APPLICATION UNIT

In this coating unit the bottom or fountain roll, preferably of soft rubber, runs partially submerged in the coating medium. Here it carries the coating to the top transfer roll.

Material being coated passes over the transfer roll with a slight contact arc which is important in controlling coating. To vary the contact arc one or both idler rolls are adjusted vertically.



...e 5. INTAGLIO APPLICATION UNIT

...pplying coatings by means of the intaglio roll, an engraved ...per roll about 6 inches in diameter is partially submerged in ...coating medium and rotates with the web at the same velocity. ...A full face laminated doctor blade wipes the excess coating ...m the intaglio engraved surface.

...he web follows the contour of the top hard rubber back-up ..., permitting an approximate line contact of the web and ...glio roll.

...hrome plating the intaglio roll after engraving adds con...rably to the life of the engraved roll.

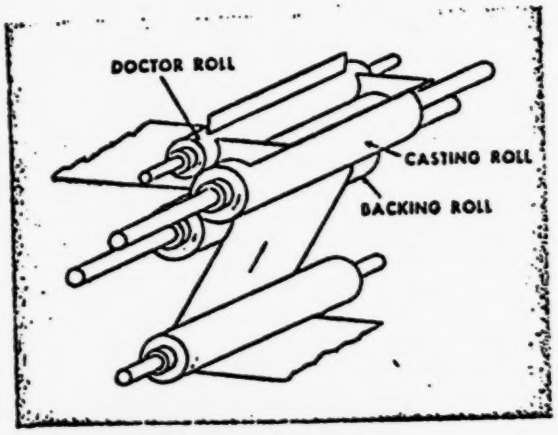


Figure 6. REVERSE ROLL COATER (Patented)

The reverse roll coating method is principally a three-roll coating unit. A backing roll rotates with the web at the same relative velocity, while a center casting roll rotates in the opposite direction to the web, casting the coating medium on the web. Here the backing roll is adjustable in relation to the casting roll.

The doctor roll, a third roll adjustable in relation to the casting roll, meters the amount of coating coming from the fountain.

APPLICATOR SYSTEMS FOR LACQUERS, ADHESIVES AND LIQUID INKS

No single method of application or type of equipment for lacquering, printing or laminating foil is commercially feasible, because choice may be dictated by conditions of foil gage, coating materials, ultimate use requirements or economy. The common methods of lacquer and adhesive application are squeegee, transfer, intaglio or engraved rolls, and reverse roll coaters. These methods are illustrated in Figs. 3, 4, 5, and 6. Lightweight coatings are usually applied by the squeegee; transfer intaglio rolls and the more versatile reverse roll coaters are the preferred equipment for heavier coatings.

DRYING EQUIPMENT FOR SOLVENT REMOVAL

Equipment for solvent removal in printing, lacquering or laminating aluminum foil may be identical in design to that used for other flexible sheets. The common and conventional type of drying is forced air convection. The heat source may be gas, steam or electricity. Important factors to be considered are the impervious, nonsorptive surface of aluminum foil, its high thermal conductivity and high reflectivity for radiant heat.

In practically all of these operations, large amounts of volatile solvents must be cared for and ample ventilation facilities should be provided for their removal. It is only safe to consider them as potential health and fire hazards. Solvents likely to be employed include alcohols, hydrocarbons, ketones, and esters of the more volatile type.

Effective means for solvent removal are: counterflow air currents, or alternate blowing and removal (by suction) of hot, dry air. Radiant heat may also be used for drying if it impinges on a surface that will absorb the heat efficiently. Since aluminum foil has a high reflectivity value (95 per cent), radiant heat should be applied to the paper or plastic side in the case of laminated sheets or on a surface to which a substantial film of ink or lacquer has been applied.

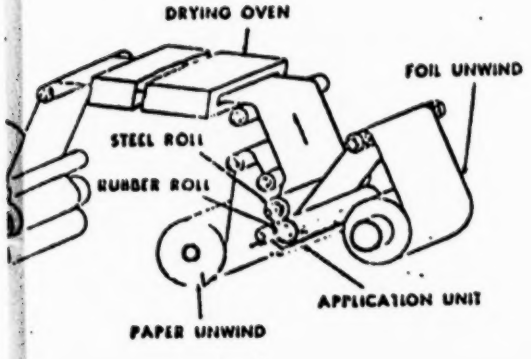
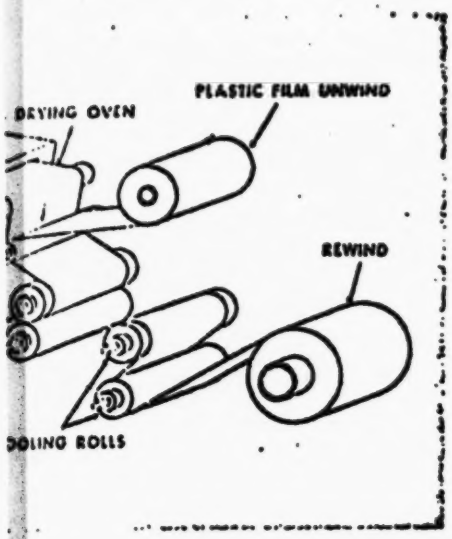


Figure 7. **COMBINING UNIT FOR FOIL AND PAPER**
In combining foil and paper, the adhesive is applied to the foil through a modified squeegee unit. A rubber transfer roll is partially submerged in the adhesive and rotates at a speed less than the relative velocity of the web. This roll runs continuously so that even when the machine is stopped the adhesive will not dry on the unsubmerged surface.

LACQUERING OR COATING, AND LAMINATING

Lacquers and other coatings are usually used for decoration, protection or to produce a heat-sealable surface and may be applied as a continuous film over one or both surfaces of the foil. Both lacquers and adhesives, which are used in laminating foil to various supporting sheets, may be applied by any one of the methods described previously. In laminating foil to paper with water soluble or dispersed adhesives, the adhesive is preferably applied to the foil by one of the methods described and the foil brought in contact with the paper web immediately after leaving the application unit, as illustrated in Fig. 7. In mounting foil to various transparent sheets and other nonporous surfaces, however, the adhesive is applied to the surface of the foil in the same manner, but the coated foil is passed through a drying tunnel to remove the solvents before the bond is effected by bringing the foil in contact with the supporting sheets between heated pressure rolls. This is illustrated in Fig. 8. In the case of both lacquered and laminated foils, cooling rolls, placed immediately ahead of the rewind unit, are used advantageously to lower the temperature of the heated web and thus prevent blocking or sticking.

In handling hot melt adhesives, a somewhat different procedure is used. The adhesive material in this case is generally applied to the surface of



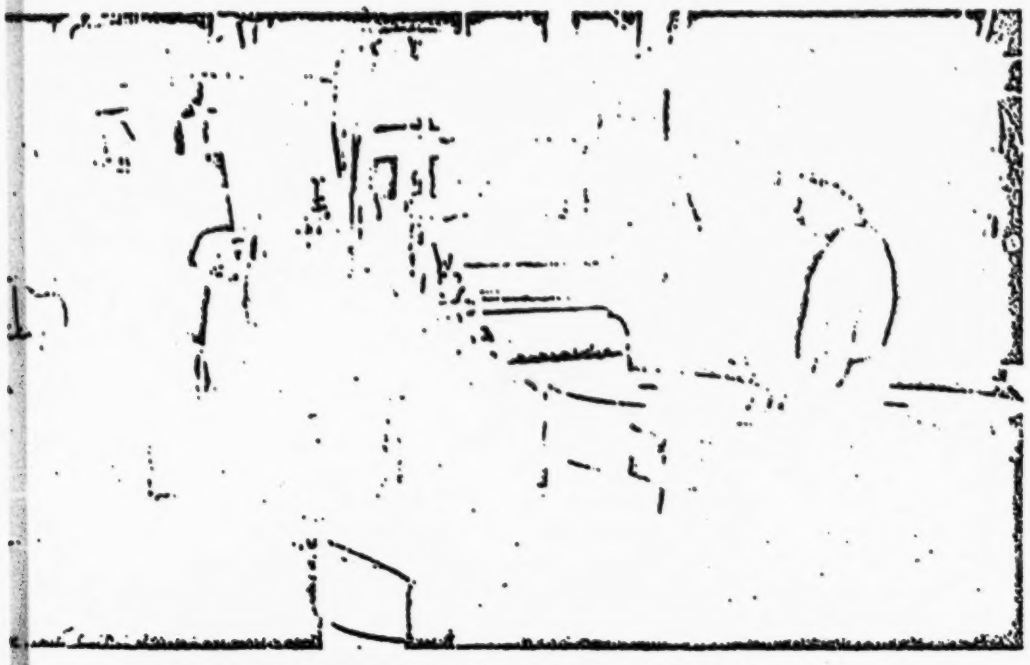
COMBINING UNIT FOR FOIL AND PLASTIC FILMS
The foil web coming from the solvent evaporating compartment combines with the plastic film and this composite is pressure set through the hard rubber and steel pressure rolls. The steel roll is heated electrically or with steam and is driven at the velocity of the composite web.
After leaving the pressure roll unit, the heated web is cooled as it passes over the double-roll cooling unit.

the supporting sheet and, after chilling, is brought in contact with the foil and bonded with the aid of heated pressure rolls. The laminated material is subsequently cooled and rewound.

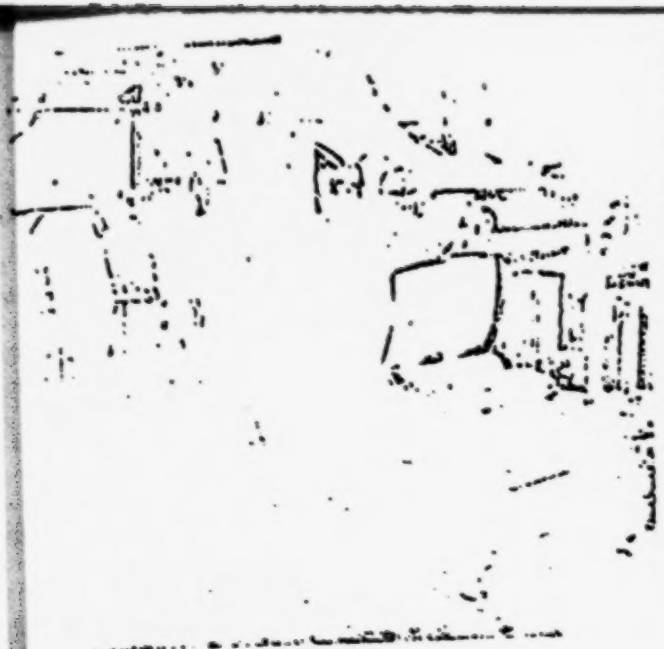
PRINTING

Aluminum foil can be printed satisfactorily by any of the accepted commercial processes which are based on the three fundamental types of printing—typographic, planographic and intaglio. Variations of these basic procedures are known in the trade as letterpress, aniline, Anilox, lithographic, silk screen, offset, gravure and rotogravure. The most commonly used and accepted methods for printing on foil are termed aniline and rotogravure.

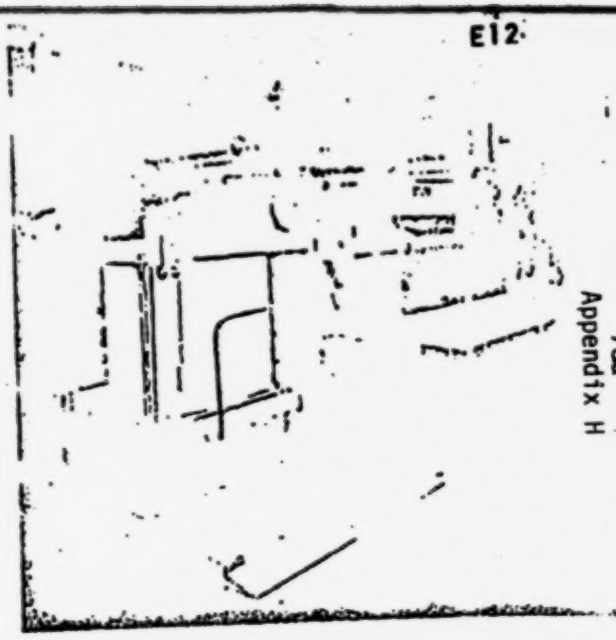
Aniline ink printing is versatile and is used in the printing of both supported and unsupported plain foils. Thin foils should be supported by paper or other cushioning sheets. This method of printing is particularly applicable for producing decorative wrappers of all kinds from coiled foil alone or foil combined with other flexible packaging materials. The drying speed of aniline inks and the ease and low cost of preparing rubber plates



This machine laminates aluminum foil to paper and slits it into multiple cuts in one operation.



A four-color aniline press shown above represents one of the types commonly used in the printing of aluminum foil and other flexible packaging materials.



Aluminum foil backed with a supporting sheet is ideally suited to gravure printing. Presses equipped with a sheeter, such as the one above, are capable of excellent performance at high speeds.

place this method in an advantageous position to handle smaller production items. Aniline ink printing is restricted in the application of its designs to foil only by limitations of the rubber plates for reproducing fine lines and halftones and by the characteristics of the ink films to meet severe requirements.

Rotogravure printing is recognized for its quality in subject duplication, color, uniformity and the wider range in tonal effects from strong, deep colors to the extremes for highlighting. It also offers operating advantages in high speed production and long production runs. Web printing by rotogravure is an economical process for the volume production of foil-paper backed labels and overwraps.

SURFACE PREPARATION FOR PRINTING

Prime or wash coatings are commonly used on laminated foils that are subsequently printed. This treatment is frequently given where adherence and durable life of the printing are stressed. Priming with a wash coat may be done in conjunction with the laminating operation or may be applied in the initial color stand of a multicolor printing press. These solutions are dilute and fast drying.

Phosphoric acid in alcohol can be used to improve the wetting characteristics of foil if the [illegible] sheet does not have to withstand water. Plasticized shellac or shellac plus a small quantity of phosphoric acid in alcohol may be used for such applications. Where water resistance is important, vinyl resins such as polyvinyl butyral may be used to advantage in formulating wash coatings.

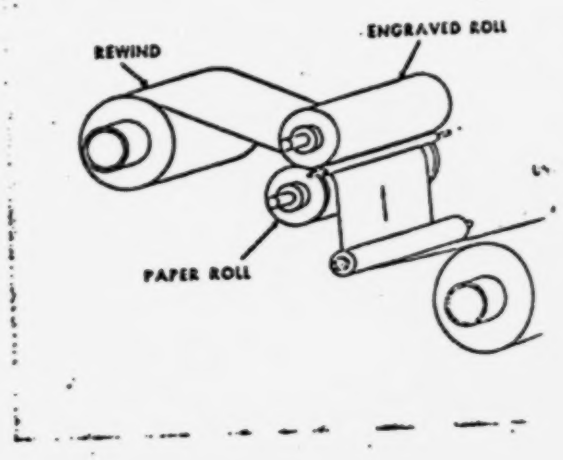


Figure 9. EMBOSSING UNIT

An engraved steel roll, usually the top roll, carries the design, and a matching paper roll becomes the matrix.

This matrix roll is constructed of layers of paper (wool rag paper) rings compressed solidly into one continuous mass with steel end rings holding it intact.

The web follows the contour of the matrix roll through the contact point of the roll set where pressure is applied between the rolls.

OSSING

e embossing of aluminum foil is normally
d out as a means of decoration, but on
ion it may be used to improve functional
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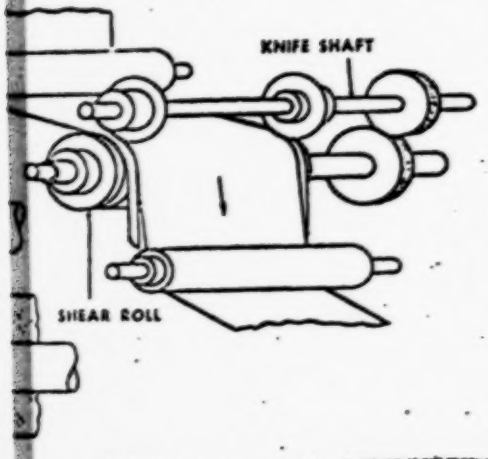
rmally, decorative embossing of thin, annealed
performed satisfactorily in continuous roll
by passing the web through a roll stand
ped with one engraved steel roll and a soft
roll of paper. Pressure for embossing may
tained by maintaining the paper roll with the
in a fixed position and using only the weight
steel roll to depress the negative pattern into
per roll. Screw or hydraulic pressures may be
d to embossing operations when necessary
rable. This is the procedure commonly used
mbossing aluminum foils or laminated foil
inations and is illustrated in Fig. 9.
inated foil combinations or heavier gage
ay also be embossed on equipment consisting
engraved steel rolls. The design is engraved
e steel roll (male) and the negative to this
on a second steel supporting roll (female).

It is essential that these steel rolls be designed and mechanically equipped to register exactly for the embossing operation. Also, the engraving and operation of the embosser must be precisely executed to avoid cutting the material or marring the engraved rolls.

SHEARING

Shearing or slitting operations are a necessary part of practically all foil converting operations. Shearing is required to produce narrow coiled widths, to trim the edges of coated or laminated stock and to produce rectangular pieces. Die cut designs by rotary or stationary die settings and shearing with flying knife cutoffs may also be included as shearing methods.

Guillotine shears are standard equipment for square shearing. Plain foil is usually interleaved with thin paper (10 lb to 15 lb tissue) before square shearing. This is done to facilitate separation of the thin foil sheets by eliminating interlocking or sticking edges, to add support and rigidity to the stacked sheets and to minimize surface marring



10. IDLER ROLL SHEAR UNIT
FOR COATED AND LAMINATED FOIL PRODUCTS

Shear unit the foil web follows the contour of the bottom roll sufficiently to rotate the unit and thus drive the top knife shaft. Gears mounted at one end of the unit a speed increaser, thereby permitting the top slitting to operate at a greater velocity than the web (approxi- 20 per cent).
bottom shear roll is assembled with heat-treated steel clamped between mild steel spacers, and the assembled ound as a unit.

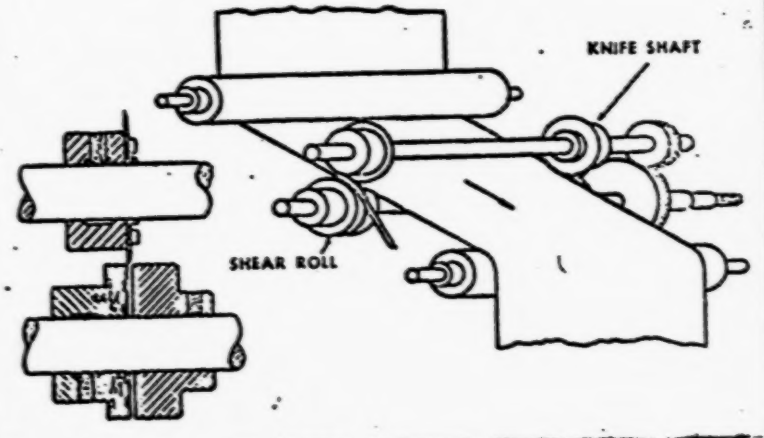


Figure 11. DIRECT SHEAR UNIT FOR COATED AND LAMINATED FOIL PRODUCTS

Material sheared by the direct shear method must be supported on both sides of the shear unit to maintain flatness of web.

The shear unit is externally driven with the bottom knives rotating with the same velocity as the web. Gears located at one end of the unit represent a speed increaser, allowing the top slitting knives to operate at a greater velocity than the web (approximately 20 per cent).

from handling and shipping. Foil in the hard condition and annealed foil when lacquered, mounted on paper or other supporting sheets, do not usually require interleaving for square shearing.

The most commonly used method of slitting or shearing laminated coiled material is the shear cut. This method of shearing is illustrated in Figs. 10 and 11. Shearing equipment must be sturdy and true to prevent weaving and avoid physical defects in the wound, slit coils. Shear knives must be properly set, firmly fixed, sharp and otherwise in good condition. Knife edges are preferably lubricated with a volatile, nonstaining material such as very lightweight white oils or kerosene.

lacquers, adhesives and inks used with aluminum foil

Many types of lacquers, adhesives and inks are used in foil converting operations, and some general information on the desirable characteristics of these materials will be given.

LACQUERS AND COATINGS

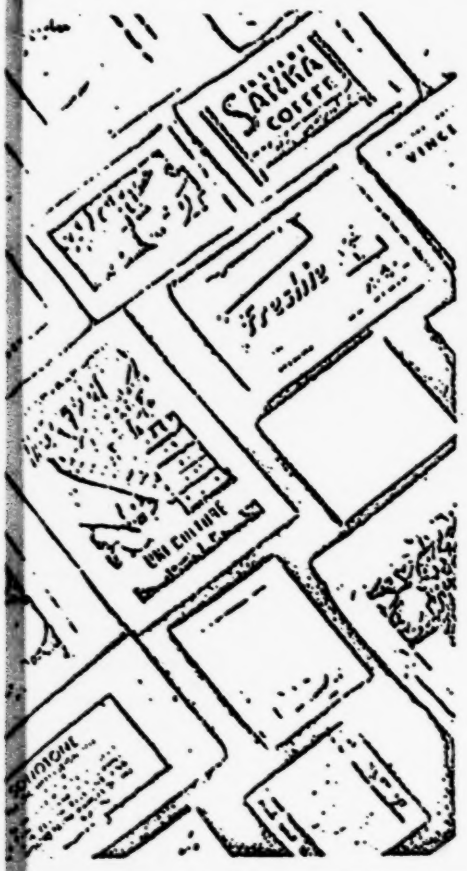
Lacquers and coatings used on aluminum foil may be classified as decorative, heat sealing and protective. Basically, each type should be characterized by good adherence and film forming characteristics. Since many of these materials may come in contact with food products, it is essential that they be nontoxic and free from any residual odor or taste.

DECORATIVE LACQUERS

Decorative lacquer formulations are expected to include resins, plasticizers and nitrocellulose. They include solvents properly blended to give a viscosity flowout and evaporation rate appropriate to the method of application and required film characteristics. Resins, both natural and synthetic, blended and plasticized are also used to produce decorative finishes. Decorative foil lacquers may be colored with dissolved dyes, dispersed lake colors, very finely ground pigments in paste or plasticizers or normal ground commercial pigments.

Decorative lacquers should be selected on the basis of their intended end use. For example, some decorative lacquers may be exposed to sunlight and for this reason color fast dyes or pigments should be used to obtain the desired color. Other decorative lacquers, such as those used in producing milk bottle hood foil, should be able to withstand a slight amount of forming and at the same time be water resistant. The lacquer films for beverage labels including color and pigments may have to resist severe exposure to an alcoholic beverage or to water immersion. When decorative finishes appear on the opposite side of foil to which a heat-seal coating has been applied, the decorative film must withstand the temperatures required for activating the heat-seal coating without becoming discolored, brittle or tacky. Film forming materials and colors of basically different characteristics may be required to obtain these distinctive film requirements.

The eye appeal of aluminum foil makes it an ideal material for ... covers and other decorative applications. It is readily lacquered, ... or embossed.



foil packets offer a high degree of protection
ppliance.

SEAL COATINGS

heat-sealing, adherence and film forming
istics are desirable for all heat-seal coat-
ials. It is also desirable that these materials,
chemical resistance since many of them will
contact with materials that may destroy
characteristics or react with the alu-
foil.

al coatings of the vinyl type are con-
to be the most satisfactory all around
for use on aluminum foil. Heat-seal
ased on cellulose nitrate, ethyl celluloses,
ylates, chlorinated rubbers and rubber
have also been used satisfactorily on
foil.

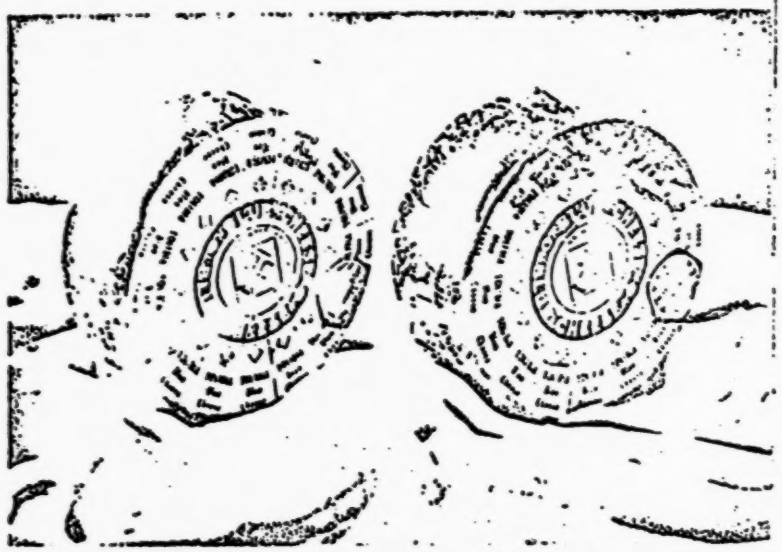
heat-seal coated foils are produced using
ings identified as S-1298 and S-1299. The
mount of Alcoa heat-seal coatings S-1298
9 applied is approximately two grams
housand square inches.

t-seal bond strength between two coated
creases slightly with increased film thick-

nesses. The thicker than normal films are used only in the packaging of small costly items requiring a maximum of care and protection. For the normal heat-seal coatings the bursting strength added to the foil by the coating is not significant. The effect of increasing the coating weight becomes important only above a coating thickness of one mil.

PROTECTIVE COATINGS

Protective coatings may be applied to aluminum foil for protection against chemical attack or against fingerprints or other handling marks, which may detract from the appearance of foil used in decorative applications. For most purposes the heat-seal coatings applied to aluminum foil act in the double role of providing heat-sealing characteristics and protection against chemical attack. For other applications, where heat-sealing is not a factor, a somewhat lighter coating weight (approximately one gram per thousand square inches) may be all that is necessary. It is usually best, however, to consider each application of this type as a separate problem and to select the coating material and coating weight best suited to meet the special requirements. Resistance to chemical attack or to mechanical abuse may also be provided by various transparent packaging films laminated to one or more surfaces of the aluminum foil.



Cheese is one of the many foods packaged in Alcoa aluminum foil to protect its quality. Such foods as cheese, which might react with plain foil, are safely packaged in foil protected with a suitable coating.

ADHESIVES

A wide range of adhesive materials is available for use with aluminum foil, but the special requirements of each job usually restrict the selection. It is necessary that the adhesive material selected adhere well to the foil surface and to the surface of the supporting sheet. Other specific requirements that may affect the choice of adhesives are color, odor, and resistance to heat, cold and moisture.

Adhesives that have been used satisfactorily in laminating aluminum foil to various supporting sheets range from water dispersed starch, casein, casein latex, sodium silicate, glucose and resin emulsions, to thermoplastics in organic solvents, waxes, asphalts and various formulated blends of these materials. For convenience, these adhesives may be classified as: (1) water soluble, emulsions and dispersions; (2) thermoplastics in lacquer type solvents; and (3) hot melts.

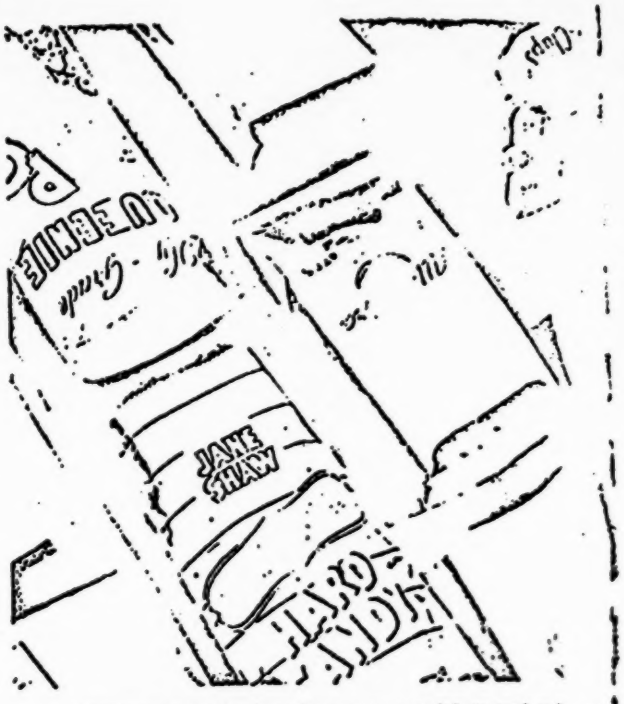
WATER SOLUBLE, EMULSIONS AND DISPERSED ADHESIVES

Adhesives of water soluble or emulsion types in general have been found to be best suited for bonding aluminum foil to papers and other fibrous materials. Since water is a natural wetting agent for papers, this aids in establishing a more permanent bond between the foil and paper for anchoring the adhesive to the outer fibers of the paper stock. Sodium silicate adhesives and starch adhesives, including blends with gums and dextrines, are relatively low priced and may be used in laminating foil to paper for cigarette wrappers, certain types of labels, box wrappers and similar products.

The casein and casein latex formulations as well as emulsions of resinous materials are somewhat more expensive, but allow greater flexibility in fields of application. These adhesives are normally used where strong bonds and resistance to water are required, as in the case of beverage labels and other similar products. As a general rule, they are more water resistant than those of the sodium silicate or starch type.

THERMOPLASTIC ADHESIVES IN LACQUER TYPE SOLVENTS

Thermoplastic adhesives in lacquer type solvents are used primarily with the transparent cellulosic and noncellulosic packaging materials. The nonaqueous lacquer type adhesives consist generally of resins, plasticizers, nitrocellulose or ethyl cellulose. Vinyls and synthetic or reclaimed rubber also may be considered in this group. Adhesives of this type are quick setting and may be formulated to give a long or short tack period after solvent removal and still retain thermoplastic properties.



Aluminum foil is laminated to many materials to produce a foil-covered bags. Effective closures may be obtained by folding, sealing, or heat sealing.

HOT MELT ADHESIVES

Hot melt adhesives used with foil include asphalt, waxes and formulated products. The formulated products may contain a relatively large percentage of microcrystalline waxes modified with latex or resins. Since hot melt adhesives do not contain solvents, drying facilities are not required in their application. Hot melt adhesives offer greater adherence and cohesive strength than does normal paraffin wax. They offer additional resistance to water vapor transfer and are generally satisfactory for use in food wrappers. Because foil may wrinkle under heat, hot melt adhesives are usually applied to the surface of the supporting sheet.

aluminum

its uses ...

s indicated earlier, aluminum foil may be printed
y of the commercial processes used on flexible
ging films. The choice of practice and inks
nds on the conditions to be met. Ink composi-
are varied to meet requirements and are best
dered as specialty items. Inks used in printing
il may be classified as aniline, intaglio and
graphic.

line inks are normally associated with the
of alcohol soluble resins, spirit soluble dyes
ubber plates. Alcohol is one of the least
ful solvents in contact with rubber and is a
solvent for dyes. Shellac is one of the most
only used resins suitable for rubber plate
g. Other alcohol soluble resins with plasti-
may be used and small quantities of alcohol
nitrocellulose can be included. Aniline or
plate printing inks may also include water
, hydrocarbon and mixed solvent formula-
along with oil soluble dyes and opaque
ts. The possible variations in aniline ink
ations along with the Anilox method of
g extend to some extent into the scope of
vure inks which, in turn, approach fast
lacquer formulations.

lio or rotogravure inks permit a wider
of resins and solvents than rubber plate or
inks. Intaglio inks for foil may be best
ed as fast-drying lacquers, formulated to
press and use requirements. Some of the
sed in formulating intaglio inks are shellac,
c, colophony, copal, dammar and synthetic
uch as vinylite, ester gum, glyptals and
s, along with nitrocellulose and other cellu-
mpounds. Solvents used with these resins
much the same type as those used with
ive lacquers. They should, however, be fast
o as to permit the immediate forming of a
, nonblocking film.

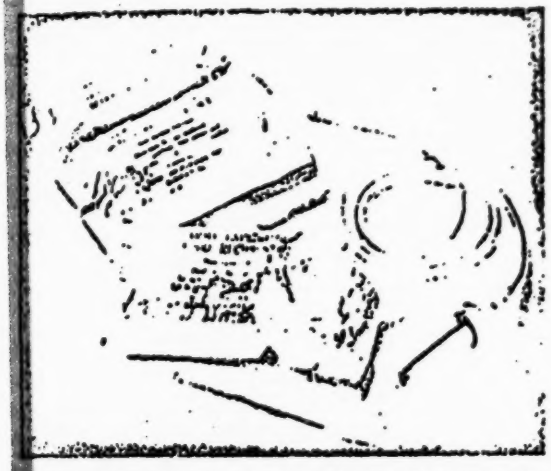
graphic or paste inks are seldom used with
m foil. They are used for printed, coiled
s where the ink is deposited in the recesses
y embossed impressions and drying is not
m. They are also used in printing square
pieces of foil supported by paper and
ard, which are interleaved and allowed to
vernight to dry. These inks normally con-
ious resins, treated and untreated oils,
, driers and modifiers, or wetting and
g agents.

aluminum foil in packaging

Aluminum foil, alone or in combination with various supporting materials, is a versatile packaging material with hundreds of applications. The basic properties of aluminum foil have been outlined in previous chapters. The principal characteristics of foil which recommend it for various packaging applications may be summarized as follows:

1. Impervious to moisture and gases (in thicker gages)
2. Greaseproof
3. Nonsorptive
4. Shrinkproof
5. Odorless and tasteless
6. Hygienic, nontoxic and substantially sterile
7. Resistant to corrosion, nonaging
8. Dead folding
9. Strong
10. Functions well in laminates
11. Appearance, brightness and glitter
12. Reflects radiant heat, opaque to light

While it is not practical to give details of every foil packaging end use, illustrations and laboratory data which support some of these applications will be presented.



Alcoa aluminum foil not only looks clean, but it is also substantially sterile. This is one reason why it is used in packaging many medical products.

HYGIENIC ASPECTS OF ALUMINUM IN PACKAGING

The fact that aluminum is nontoxic and friendly to foods makes it an entirely safe packaging medium. This fact has been established not only by scientific

A wide variety of packaging applications attests the versatility of Alcoa aluminum foil.

The bright appearance and protective qualities of Alcoa aluminum foil make it a favorite material for packaging confections.

...on, but also by long experience, particu-... aluminum cooking utensils. Carefully ... tests have proved that contact with ..., in contrast with the effect of certain ...ds, does not accelerate the loss of vitamins ...g. The loss of Vitamin C during the ...ion of milk in an aluminum container ...greater than when pasteurized in contact ... The loss resulting from heating under ...itions was about 30 per cent, while the ...tion of milk in copper completely de-...amin C. This is only one of the reasons ...num foil closures have proved so satis-... the bottling of milk.

...ACKAGING

...m foil as part of wrappers, bags, cartons, ...ntainers and hermetically sealed packages ... is used in the packaging of a large ... food products. As such, there isn't a day ... luminum foil does not enter the homes ... in one form or another. Some of the ... products that are satisfactorily packaged ..., cheese, oleomargarine, frozen foods, ..., dehydrated vegetables, potato chips, ...sserts, chewing gum, confections and ...ood mixes.

Tablo 6

RESULTS OF STORAGE TESTS OF WRAPPERS FOR CHOCOLATE NUT CANDY BARS

DESCRIPTION OF WRAPPER	Condition after 25 days' storage at 85-90° F		
	Weight loss in grams	Flavor rating*	Appearance rating*
1. Aluminum foil (0.001") coated with heat-sealing lacquer and laminated on opposite side to acetate sheeting; lacquer coating next to chocolate. This wrapper was heat sealed at seams and ends.	0.5	1	1
2. Aluminum foil (0.001")	1.5	2	2
3. Aluminum foil (0.00045") laminated to waxed glassine paper (0.0015"); waxed glassine paper next to chocolate.	2.5	2	3
4. Waxed paper (0.0022") separate inner wrap; overwrap of aluminum foil (0.00045") wax-laminated to glassine paper (0.0015").	2.5	2	3
5. Aluminum foil (0.00045") laminated to glassine paper (0.0015"); glassine next to chocolate.	2.5	3	3
6. Waxed paper (0.002") separate inner wrap; glassine paper (0.0015") overwrap.	11.0	4	4

*In flavor and appearance, No. 1 is the highest and No. 4 the lowest rating.

CONFECTIONS

The protection of a good wrapper is important in maintaining the quality of items such as chocolate and chocolate candy bars, which should reach the consumer in the freshest possible condition. This means the appearance should be appetizing, texture correct and flavor free from staleness or rancidity.

Figure 12

These two rolled rib roasts were both held in a freezer at approximately 0°F for six months. The one shown in the top picture was wrapped in aluminum foil and the other in waxed parchment freezer paper. The foil wrapped roast retained its freshness while the other developed freezer burn as indicated by its white porous surface.

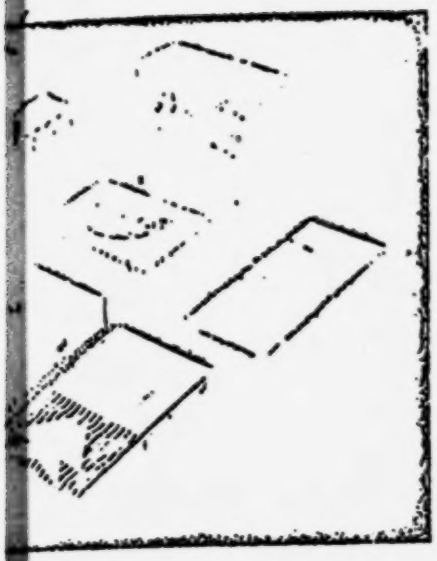
In Table 6 are data from storage tests of chocolate nut bars wrapped in six different types of wrappers and stored for twenty-five days. Performance of these wrappers was judged in several ways: by the weight loss after twenty-five days' storage, by the flavor and by their appearance. The flavor and appearance ratings were appraised individually by three different inspectors. The chocolate nut bar wrapped in plain waxed paper with a glassine outer wrap showed the largest weight loss after storage. This same bar also had an important loss of flavor and appearance. It was distinctly stale in taste and appeared hard and dry with surface crumbling along the edges. Mold was not observed on any of the chocolate bars. Wrapper No. 1, which was a laminated foil wrap with heat seal showed the best performance on all counts. However, all the chocolate bars in the wrappers that employed aluminum foil had a soft creamy texture and were free from staleness. In the case of chocolate and other products where volatile essential ingredients play an important part in flavor and palatability even a very small weight loss may be significant in loss of quality.

It is also important to employ a wrapper that will prevent the absorption of foreign odors by chocolate. A severe laboratory test was carried out in which several milk chocolate bars wrapped in various ways were stored in desiccators containing, in one case, cotton moistened with turpentine, and in another, strong peppermint candy. At periodic intervals the bars were removed, unwrapped and tasted by two or more inspectors in order to determine the first trace of turpentine or peppermint vapor absorption. Results of these tests, shown in Table 7, show definitely that while it was only a matter of hours before the paper wrappers permitted the absorption of foreign odors, the aluminum wrapper kept the odor out for days.

FROZEN FOODS

The packaging of frozen foods places special requirements on the wrapper. The extremely low humidity maintained in the frozen food locker and the long storage periods necessitate a relatively impervious wrapper if desiccation of the product and freezer burn are to be prevented. Storage periods may be as long as twelve to eighteen months.

Aluminum foil wrappers and foil lined cartons are being used effectively in the protection of frozen



wrappers and liners are used effectively in the
oisen foods against the loss of moisture and flavor
orage periods at low temperature and humidity

vegetables. By way of illustration, two
roasts, one of which was wrapped in
foil and the other in waxed parchment
per, were held in a freezer at approxi-
F for approximately six months. Fig. 12
results of this test. The roast wrapped in
foil lost only 1 per cent weight and was
dition for appearance and taste whereas
apped in the freezer paper had lost ten
weight and suffered freezer burn and
in quality.

EGETABLES

aging of fresh vegetables to prolong
life requires the maintenance of their
ontent to preserve freshness and pal-
Green vegetables, in addition, require a
ount of oxygen for respiration if they
succumb to wilt. Carrots are one of the
ables to keep. The following test how-
ates graphically the benefits of protective
Carrots for this test were taken fresh
rden, tops were removed and the carrots
ed. Some of the carrots were packed
rectangular, heat-sealed aluminum foil
bag. This sealed bag was placed in a
refrigerator and beside it were placed

Table 7

EFFICIENCY OF WRAPPER IN PREVENTING FOREIGN ODOR ABSORPTION BY SWEET MILK CHOCOLATE BARS*

DESCRIPTION OF WRAPPER	Time to taste	
	Turpentine	Peppermint
1. Aluminum foil (0.0007") coated with heat-sealing lacquer and laminated one side to moistureproof cellophane; coated surface heat sealed along side seam and ends	20 days	19 days
2. Aluminum foil (0.0007") coated with heat-sealing lacquer; wrapper heat sealed along side seam and ends	6 days	7 days
3. Plastic bleached greaseproof paper 22½#; side seam and folds not sealed	5 hrs	3½ hrs
4. Opaque greaseproof paper 30#, side seam and folds sealed	5 hrs	3½ hrs
5. Control—no wrapper	½ hr	1 hr

*Chocolate bars stored in glass desiccators, one containing cotton moistened with turpentine and the other containing peppermint candy.

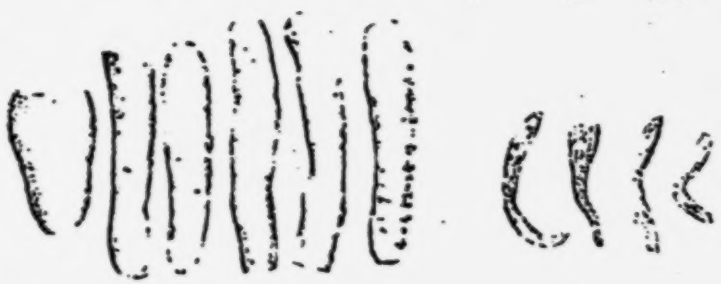


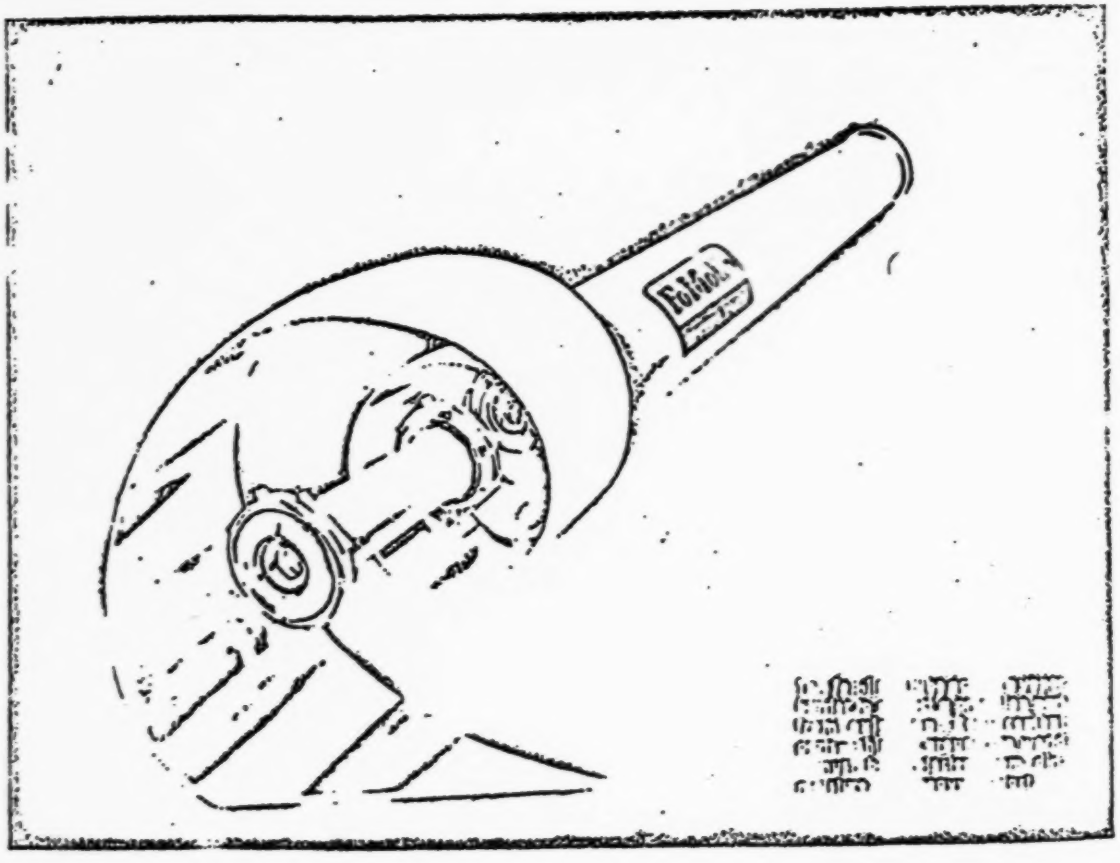
Figure 13
Comparison of carrots after 51 days' storage in a home refrigerator. Carrots at the left were wrapped in Alcoa Aluminum foil; those illustrated

These packages are produced on one of several different styles of heat-sealing equipment. Equipment design, stability and accuracy of construction are factors contributing to efficiency and economy in packing individual packets and small heat-sealing pouches.

ALUMINUM FOIL IN INDUSTRIAL AND MILITARY PACKAGING

Military requirements for export shipments and storage under tropical or arctic conditions stimulated the development of methods of packaging and the tests of packages for overseas shipments. These methods have led to changes in practices for both commercial export shipments and packaging and storage for domestic commercial activities. Aluminum foil has been used in these packaging developments primarily as part of a laminate, but plain foil is also used to advantage for water resistant, greaseproof wrappers. Flexible laminated wrappers containing aluminum foil are available in great variety. The following typical laminates indicate the numerous combinations that are made practical by varying component materials and their thicknesses:

1. Plain foil *plus* paper
2. Heat-seal coat *plus* foil *plus* paper
3. Heat-seal coat *plus* foil *plus* paper *plus* cotton sheeting or scrim
4. Heat-seal coat *plus* foil *plus* plastic film
5. Heat-seal coat *plus* foil *plus* plastic film *plus* cotton sheeting or scrim
6. Plastic film *plus* foil *plus* plastic film
7. Plastic film *plus* foil *plus* plastic film *plus* cotton sheeting or scrim
8. Plastic film *plus* foil *plus* paper
9. Plastic film *plus* foil *plus* paper *plus* cotton sheeting or scrim
10. Plastic film *plus* foil *plus* cotton sheeting or scrim



The selection of a specific sheet may be determined by government or industrial specifications or economic considerations.

Laminated foil wrappers may be used for sealed or unsealed wraps. They are used to produce bags for packaging items as large as airplane motors. Sealed bags are used alone and inside or outside of paper cartons or boxes. Very tough, strong foil-lined bags are used on the outside of fiberboard boxes so that they will withstand service abuse. Foil-lined tubes and other rigid containers are also used for protective packaging.

Packaging materials incorporating foil protect automobile accessories and parts from corrosion. They have been used on such items as cam shafts, starters, oil filters, oil cells, adapters, adjustable nut locks, gaskets and valves. Service groups have used foil laminated bags for the packaging of electronic equipment, radio and radar equipment, spare machinery parts, pharmaceuticals, camera supplies, hypodermic syringes, scalpel knives and sterilized bandages. Foil barriers protect not only by keeping moisture out, but also by keeping preservative gases on the inside.

The use of aluminum foil as a packaging material in this field is best illustrated by the results from a series of tests on wrappers for polished carbon steel bearing races. The results of this test are shown in Table 9. The first two wrappers, Nos. 1 and 2, employ aluminum foil and were very effective in the protection of oiled bearings during storage in a hot, humid atmosphere. Even wrapper No. 1, which was not heat-sealed, did a good job on the oiled bearings. The same wrapper around a dry bearing (No. 3) did not provide complete protection. It would appear that wrapping paper took up moisture and stimulated the corrosion of the steel with which it was in contact. However, foil laminated to paper greatly reduces the rate of moisture pickup and prolongs the protective life of the wrapper. The principles involved in many of the materials packaged and the experiences obtained in the packaging for export shipping by the Military Services are applicable to industrial packaging, shipping and storage problems. Therefore, it is not only reasonable but almost a necessity that many metal products and other articles requiring storage in a controlled environment will be protected with aluminum foil in future commercial packages.

Table 9

RESULTS OF STORAGE TESTS OF WRAPPERS FOR POLISHED STEEL

(Polished carbon steel bearing races, dipped in antirusting oil, excess oil drained and bearings wrapped. Packages stored at 106° F and 90-92% relative humidity.)

DESCRIPTION OF WRAPPER	Degree* of tarnishing after	
	Storage 180 hrs	Storage 1,000 hrs
1. Aluminum foil (0.00035") laminated to 25# red paper with wax; foil next to bearing	0	0
2. Aluminum foil (0.00035") laminated to 25# red paper with wax; foil next to bearing; steel bearings wrapped in foil laminate and heat sealed in bag made from aluminum foil (0.001") with lacquer coating	0	0
3. Aluminum foil (0.00035") laminated to 25# red paper; same as No. 1, except bearings were dry (not oiled); foil next to bearing	1	2
4. Red paper, 25#	1	7
5. Kraft paper, waxed	2	7
6. Waxed paper, 40#	2	9
7. White glassine	10	10 (plus)

*The degree of rusting is indicated by code numbers from 0 to 10. Zero indicates no rusting, while the degree increases from 1 to 10. No. 5 indicates appreciable rusting, while No. 10 indicates a surface which is about 90% rusted.

E24

Table 13

GENERAL FABRICATION LIMITS FOR VARIOUS TYPES OF ALCOA FOIL

Type	Grade	Gages, inch	Coiled widths, inches	Tempers
Foil	BEIS	.00025 to .0003	⅛ to 24	O or H19
	BEIS	.00035 to .005	⅛ to 53	O or H19
	CCIS	.0005 to .005	⅛ to 36	O or H19
	3S	.0007 to .003	⅛ to 36	O or H19
	3S	.003 to .005	⅛ to 48	O or H19
	24S	.002 to .005	⅛ to 20	O or F
	52S	.001 to .005	⅛ to 20	O or F
...ored, ...r decorative	BEIS or 3S	.00035 to .001	⅛ to 25½	O
	BEIS or 3S	.001 to .005	⅛ to 26½	O
...sive Coated, ... side	BEIS or 3S	.00035 to .001	⅛ to 25½	O
...sive Coated, ... sides	BEIS or 3S	.00045 to .001	⅛ to 25½	O
...l Coated, ... tinted:				
...rmal Coat, 1 side	BEIS or 3S	.00045 to .001	⅛ to 25½	O
...rmal Coat, 1 side	BEIS or 3S	.001 to .005	⅛ to 26½	O
...rmal Coat, 2 sides	BEIS or 3S	.001 to .005	⅛ to 26½	O
...uble Coat, 1 side	BEIS or 3S	.001 to .005	⅛ to 26½	O
...avy Single Coat, ... side	BEIS or 3S	.001 to .005	⅜ to 26½	O
...ssed	BEIS or 3S	.00035 to .0015	⅛ to 26	O

NOTE: Maximum length of rectangular foil: 42 inches.
Information on sizes and grades not listed is available upon request.

...RCIAL TOLERANCES Thickness or ...rea, plus or minus 10%.
...inches or over, plus or minus 1/32 inch.
...der 12 inches, plus or minus 1/64 inch.
...r, width and length, plus or minus ...
...tems under 5,000 pounds, plus or minus ... Shipping, items 5,000 pounds or more, plus or minus 5%.

CONVERTERS will supply Alcoa Foil, mounted to paper, paperboard or transparent sheeting by adhesives, wax or glue lines; lacquered, embossed, printed, etc. in form of coiled or flat wrappers, overwraps, labels, bags, envelopes, pouches, packets, covered or lined cartons, etc.

SURFACE FINISH

Single sheet rolling results in a bright finish on both sides of foil.

Pack rolling results in one side being bright and the other side dull finish. Dull finish is also referred to as "mat" or "satin" finish.

Gages .0007 inch and lighter are normally pack rolled.

Gages over .001 inch to .005 inch are normally single rolled.

Gages over .0007 inch to .001 inch may be either single or pack rolled, depending on width, plant of manufacture or customers' preference.

Table 14

STANDARD SPLICES FOR ALCOA FOIL*

GAGES	WIDTHS	TYPE OF SPLICE
PLAIN SOFT *(Annealed)* FOIL:		
.00025" to .0003"	All widths	Mechanical knurl
.00035" to .001"	Under 10"	Mechanical knurl
	10" and wider	Heat-seal foil tape
.0015" to .003"	All widths	Electric weld
.0035" to .005"	All widths	Lapped in loose ends (Electric splice if requested.)
PLAIN HARD *(Not Annealed)* FOIL:		
.00025" to .00035"	All widths	Adhesive tape
.0004" to .003"	Under 10"	Electric weld
	10" and wider	Adhesive tape
.0035" to .005"	All widths	Lapped in loose ends (Electric splice if requested.)
HEAT-SEAL COATED FOIL:		
.002" and lighter	All widths	Heat-seal coating used to splice overlapped ends
Over .002"	All widths	Adhesive tape
LACQUERED *(Except Milk Bottle Foil):*		
Under .001"	All widths	Gutta percha, heat-sealed
.001" and over	All widths	Adhesive tape
MILK BOTTLE HOOD FOIL *(Plain or Lacquered):*		Ends not spliced
ADHESIVE MOUNTED OR EMBOSSED:		
Under .001"	All widths	Gutta percha or two sides coated adhesive tape
.001" and over	All widths	Adhesive tape
WAXED PAPER BACKED:		
.00065" and lighter	All widths	Ends overlapped—wax adhesive
Over .00065"	All widths	Adhesive tape

*Ends in coiled material are spliced by standard methods indicated above unless otherwise instructed. Customers' special instructions will be complied with when requested, if possible.

EXHIBIT BV - ARTICLE - "COATINGS AND COATING METHODS FOR ALUMINUM FOIL" - 1955

...tings and Coating Methods for Aluminum Foil

The types of coatings used for foil, their purposes and applications; methods of application and coating techniques are discussed.

By I. O. ROBERTSON, JR.

Reynolds Metals Company

...IN A ...S OF ...D ON ...

THE VERY substantial increase in aluminum foil production in the past few years has naturally increased the number of problems encountered in its ...t conversion. In the early ...il converting, its end uses ...re in number as compared to ...ed usages, and consequent... problems of converting were ...plex.

...ere a number of applica... as there are now where ... foil did not have to with... pressure abuse, and con... was used unsupported. ... because of the fragile na... light gauge foil, it was often ...ellent to laminate the met... ...er for support. The paper ...ack could be handled with ...ore ease than the non-coated ... permitted more universal ... of foil. If unlaminated foil ...il, its gauge would have ...e greater in order to with... normal handling, and because ...luminum would not have ...mical.

...dhesives used originally for ... paper to the foil were ...ch. These starch adhesives ...ndedly satisfactory because ...mitations in adhesion and ...stance. As foil production ...d became more apparent ...n physical properties would ...e more accentuated into the lam... ...ion due to presence of adhe... ...wider variety of end uses, ... problems of coating tech... ...d the physical characteris... ...e coating and adhesives ...ere pronounced.

...ings can be classified into various types. There are the thermoplastic and thermosetting ones which are applied from solvent solutions. There is also the group applied from 100 per cent solids, commonly referred to as hot melts and waxes.

Thermoplastic coatings generally require only a sufficient quantity of heat to volatilize the solvents used to dissolve the solid components of the coating, whereas thermosetting coatings require heat not only to remove the solvents from the lacquer film but also to convert the coating to obtain its maximum physical properties. Thermoplastic coatings will be tack free to the touch immediately upon removal of the solvents and cooling of the web to room temperature. Thermosetting coatings will remain tacky after the solvent has been removed and until the resin components have been polymerized, oxidized, and/or cross linked by continued heating. A thermoplastic coating is sensitive to heat at any time the temperature approaches the softening point of the resin components of the coating. A thermosetting coating once solidified is an insoluble, infusible mass that no longer softens appreciably below its temperature of decomposition.

Thermoplastics

Of these two types of coatings, the thermoplastic is used more extensively

Some typical coated foil uses. Cream cheese and oleomargarine wraps are coated on both inside and outside to protect aluminum from corrosive action of cheese and oleo. Cleanser label has an overcoat to protect inks from stuffing. Aluminum tray is coated to prevent corrosion of tray from packaged goods. Two envelopes in center employ coatings on inside foil surface for protection and for hermetically sealing. Cap at bottom left is a milk bottle cap. Small bottle at bottom center has coated aluminum closure that withstands autoclaving without discoloration. Tree in lower right hand corner is coated to prevent corrosion of a...num during lamination of the various segments.

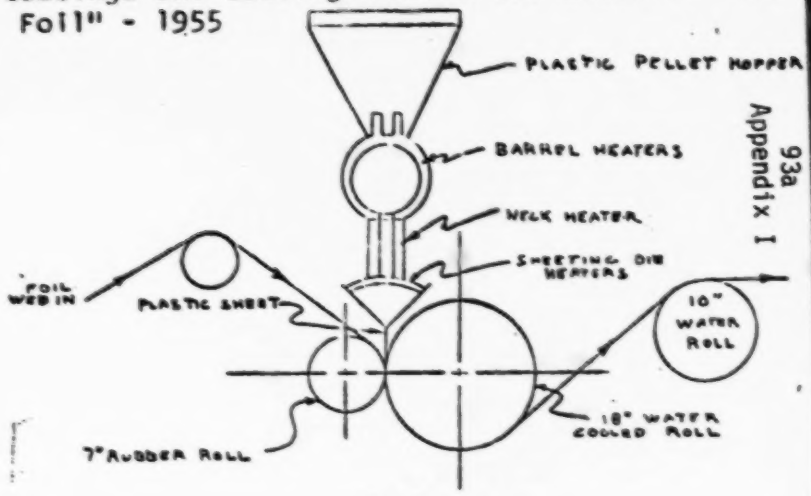


Figure 1
POLYETHYLENE EXTRUDER

by foil converting. This type does not require as large a capital outlay for equipment as does the thermosetting coatings. A thermoplastic coating is usually composed of a film former, a plasticizer, a modifying resin, and in many instances a colorant. The following film formers are used for this type of coating in varying degrees: nitrocellulose, ethyl cellulose, vinyl chloride vinyl acetate-maleic anhydride copolymer, polyethylene, vinyl butyral, cellulose acetate, cellulose acetate butyrate, vinyl chloride, vinyl acetate, vinyl chloride-vinyl acetate copolymers, chlorinated rubber and vinylidene chloride.

Of these resins, the first four are the most widely accepted, with the nitrocellulose and vinyl polymers being used most extensively. There is a tremendous number of plasticizers and modifying resins that can be incorporated in nitrocellulose solutions to give them almost any desired physical properties. Nitrocellulose coatings are used on foil for such finished products as gift wrap, florist foil, seal and label stock and many other items.

Dyes and Pigments

For many applications the nitrocellulose coating decorates the foil surface, and consequently, it must be colored a variety of shades. These colors are developed in two ways, namely, by the incorporation of dyestuffs or pigments into the coating. The end use will determine whether a dye or pigment is used. However, a general classification would be dyes for brilliance and transparency when light fastness is not a requirement, pigments when light fastness is important. The pigments do not provide as transparent a film as dyes, although certain selected pigments are very close to dyes in this characteristic. Pigments are also desired to develop certain deep shades such as greens, blues, purples, opaque oranges, yellows and black and white.

The use of dyes is most preferred because of the ease of adding them to a clear lacquer. Dyes, whether they be alcohol or oil soluble, are merely dissolved in the appropriate solvent, and added to the clear lacquer. Pigments on the other hand require mechanical working to get them properly dispersed into the lacquer resins. The equipment used for this dispersion include pebble or ball mills, three-roll or five-roll ink mills, bambury grinders, or two-roll mills.

Overcoatings

There are instances where colored coatings have to be protected against excessive abrasion. This protection requires the use of a clear overcoat. In determining the type of overcoat, consideration must be given to the effect of the solvents in the overcoat on the nitrocellulose or other types of coating used. The most universal overcoat used for nitrocellulose is formulated with an ethyl cellulose film former. The solvents necessary to dissolve ethyl cellulose are not active solvents for nitrocellulose and therefore bleeding or insipient lifting is no problem.

Ethyl cellulose is also used by itself as a coating for aluminum. This film former, being soluble in a blend of solvents with a very high hydrocarbon content, is especially adaptable to metals with a slight residual oil film on the surface. The hydrocarbon has a tendency to wash the metal and thus enhance the adhesion of the ethyl cellulose to the foil. This coating can be used for the same purposes as the nitrocellulose and, in addition, in applications where resistance to mild alkali is required.

Vinyl Polymers

For the best protection against acidic and alkaline products, the vinyl polymers are most generally employed. The vinyl polymers cover a wide variety of resins, but there is only one that has the desired properties for a foil coating. The vinyl acetate, vinyl chloride polymers and copolymers do not have good adhesion to aluminum. Consequently, a vinyl tripolymer tailor-made to have adhesion to aluminum has been adopted. This resin has excellent adhesion to aluminum and, when stabilized properly, finds a wide variety of uses. It is employed most frequently to protect the aluminum foil from certain types of moist, fatty, and highly seasoned products. It also finds application in the decorative field when the coated foil is to be subjected to outdoor exposure.

Polyethylene

The resin which is having the most rapid growth as a coating for aluminum today is polyethylene. This inert

Meet the author . . .

I. O. Robertson, Jr. is a graduate of Virginia Polytechnic Institute, having received a BS Degree in Chemistry. He attended graduate school at the University of Virginia for two years. For the past eleven years he has been associated with the Research and Development Department of the Reynolds Metals Company, concentrating on the development of inks and coatings for aluminum foil. For the past several years he has been Head of the Plant and Sales Service Group. This group has as one of its responsibilities, the development of papers, adhesives, inks, coatings, used in conjunction with aluminum foil.

g alloids protection under prac- all conditions including those freezing temperature. It can be used as a sealing media to ...kes or envelopes

...thylene foil combinations are ...e wide acceptance in the food ...aging industry. This film forms ...xcellent heat sealing media in ...tion to protecting the foil from ...k in most packaged products.

...ith the present emphasis on long ...storage of military articles, poly- ...ene is finding extensive use as a ...ponent of foil packaging materials. ...ves both as a heat sealing media. ...also as a laminate to bond a ...n cloth to the outside foil surface. ...plication of this type withstands ...temperature exposures of -70- F. without becoming brittle and ...temperatures of 160-deg. F. ...out blocking. A combination of ...thylene film, aluminum foil, and ...n cloth is now being used suc- ...fully to meet certain rigid require- ...ts of the armed services.

Extrusion Coating

Polyethylene, being an inert mate- ...l cannot be applied to the metal ...the same manner as the film form- ...mentioned previously. It has to be ...ied from a molten state. At first, ...s presented an application problem ...only the very low molecular weight ...mers could be applied with the ...mal hot melt equipment. The low ...lecular weight polymers have very ...r film characteristics, and there- ...e are of no practical value when ...d alone.

A new coating technique, molten ...trusion, was developed for applying ...gh molecular weight polyethylene ...ich possesses all of the desired ...n forming properties. Essentially this ...ess consists first of introducing ...nulated polyethylene into a hopper. ...e resin is carried by a screw ...ough a heated chamber maintained ...ove the melting point of the resin. ...As soon as the polyethylene becomes ...id, it passes through screens, down ...chamber perpendicular to the ...reen, and into a die. The opening ...the die is maintained anywhere ...tween three to ten thousandths of ...an inch, depending upon the gauge ...f film desired. The back pressure ...forces the molten polyethylene ...ough the die opening. Very near ...he opening, the foil and film are ...rought together under pressure with ...an excellent bond being secured. As ...there are no solvents to be removed ...from the extruded film, high speeds ...can be maintained on the equipment. (*See figure I.*)

In any review of foil coatings, con- ...sideration must be given to the tech- ...niques of coating and the problems involved. The equipment used in foil coating is specially designed for high speed production. The coatings therefore must be formulated to allow almost instant release of the solvents.

There are various methods for applying a coating to the surface of the metal. The one most used today employs the rotogravure principle. The coating to be applied is formulated with low viscosity resins to permit the application of a high solids coating at the proper solution viscosity. The solids of the coating is an important factor for it affects the quantity of coating that will be retained on the foil surface after evaporation of the solvents in drying. However, a characteristic even more important than the solids, is viscosity. The rotogravure principle is developed around the viscosity of the coating to be used, for it controls the uniformity of the coating on the foil surface.

Rotogravure Coating

For rotogravure applications, the coating is placed in a pan at a predetermined viscosity. A machined or etched cylinder, commonly classified as a knurl, revolves in the pan of lacquer. (*See figure II.*) The coating knurl has been mechanically or photographically worked with a design developed for coating. The three most prominent designs are termed as quadrangular shape cells, triangle-helix shape cells, and line screen. A cylinder having quadrangular shape cells is composed of a number of cells systematically arranged and worked to a specific depth, dependent upon the quantity of coating to be applied.

There are a range of quadrangular shape cell designs available, varying from a No. 10 with a depth of .017 inches, and using 132 cells per square inch, to a No. 304 with a depth of .0000 inches, and using 47,089 cells per square inch. One of the designs used on foil is a 120 quadrangular shape cell having 6,724 cells per square inch of surface area with a cell depth of .0032 inches. This knurl will apply approximately five pounds of 100 percent solids coating per ream to the foil.

In foil converting various ream boxes are employed, one of which is 480 sheets, 24 by 36 inches in size. This ream has an area of 414,720 square inches. On all coatings applied from a solvent system, the quantity of coating to be applied to the metal can be calculated. For example, using a 120 quadrangular shape cell, a 25 per cent solid lacquer will apply approximately five pounds of wet lacquer and therefore 1.25 pounds of dry film per ream.

A triangle-helix shape cell knurl is composed of a series of hills and valleys, and the designations are numerical. For example, a knurl using 84 triangle-helix shape cells will have 84 hills and valleys to the linear inch of surface area running diagonally around the circumference of the cylinder. The depth of the cell in this particular design is .0039 inches, having an angle of 36-deg. There are a range of triangle-helix shape cells ranging from a No. 24 having a depth of .014 inches, and a cell angle of 38-deg. to a No. 120, having a depth of .0022 inches with a cell angle of 45-deg. A knurl having the 84 triangle-helix shape cell design will apply approximately 10.5 pounds of a 100 per cent solids coating, thus a 25 per cent solids coating will apply 2.5 pounds of dry coating to the foil.

A line screen knurl or printing cylinder, as it is more commonly termed, is not a machined cylinder but is photographically etched. It is composed of cylindrical cells which are etched to a specified width of cell to width of wall ratio. For example, a 3-1 cell to wall ratio refers to a cell that is three times the width of the cell wall. The normal depth of the cells vary between .001 and .0015 inches. The width of the cell wall determines to a great extent the depth

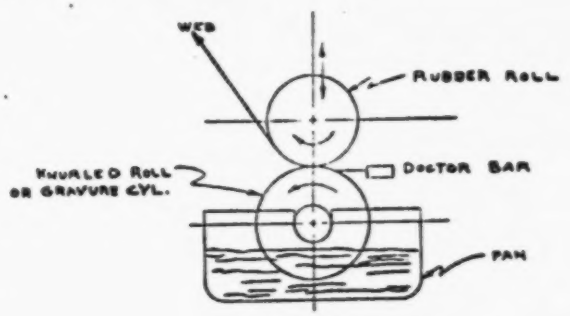
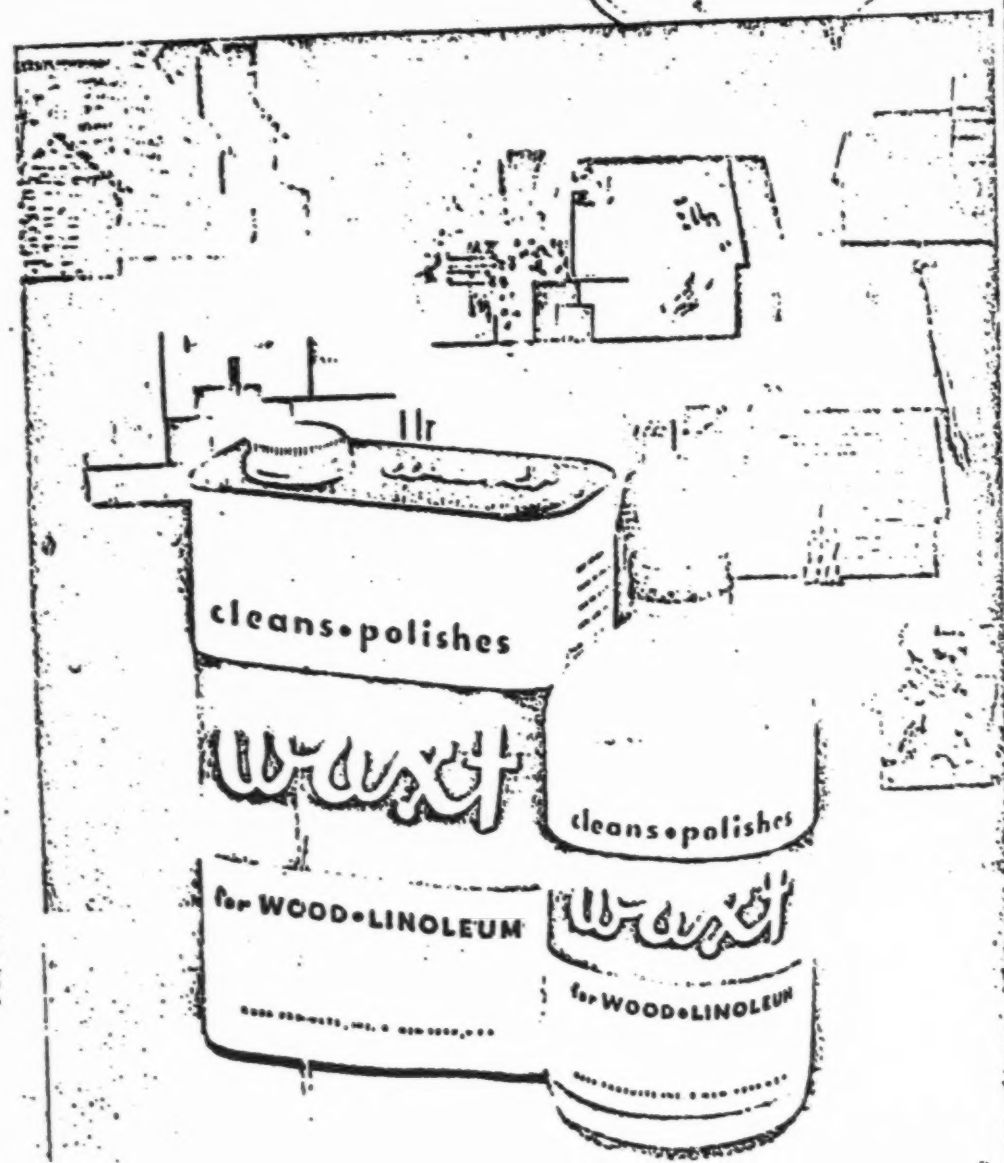


Figure II
GRAVURE TYPE COATER

Modern Packaging



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the 15th of each month by Mod-
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e this issue, 50¢ per copy.
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et of June 5, 1934, at Easton,
ized October 7, 1936.

PACKAGING is regularly in-
the *Industrial Arts Index*.

THE PACKAGE SMASHERS

"THE POSTAL AUTHORITIES," said a recent letter to our Reader Service, "have developed their package-smashing machinery to such a high degree of technical efficiency that we are forced to look to you for help."

We could only suggest to this reader that he purchase the best possible shipping-package materials, cushion his product carefully and hope for the best. Apparently the Post Office Department takes the same view.

After numerous complaints, the Toilet Goods Assn. recently conducted a canvass of members which revealed a staggering increase in parcel-post loss and damage in the last year. A letter to the Post Office Department brought a reply pointing out that there has been an unprecedented volume of shipments in recent months; that unavoidable congestion and delay at transfer points has resulted and—in effect—that faith should be put in the package and not in the tender care of overworked mail handlers.

Soaring loss and damage figures are not peculiar to parcel post, but are noted in every type of shipment—and, with the enlarged European-aid program putting new strains on our transportation system, the situation is likely to get worse before it gets better.

Fortunately, good quality shipping-container and packing materials are once more available. The place to attack the shipping-loss problem is in your own shipping room. Stay away from inferior packaging materials. Make sure that extra cushioning is provided at all points of immediate contact with outside shock. See that your products are so securely protected as to withstand the most brutal kind of handling—because that's what they're going to get for a long time yet.

The Editors

TECHNICAL
ENGINEERING & RESEARCH DEPARTMENT

LUMINUM FOIL

I—Its properties for packaging

By JUNIUS D. EDWARDS* and D. B. STROHM†

ordinary progress has been made in recent
rs in applying the tools of science and the
of research to the art of packaging. No longer
ducts be merely wrapped or placed in con-
The hazards of storage and shipment can be
l reliably and the package designed and con-
to afford adequate protection. In the solu-
the problems facing the packaging industry,
n foil has been extremely serviceable. Devel-
in this field continue under the impetus of
y and plant investigations. This article will
summary of up-to-date information on the
nt properties of aluminum foil in the various
which it is employed for packaging.

ical properties

num foil is, in effect, aluminum sheet which is
0.006 in. in thickness. For packaging, the
mmonly used gauges run from 0.0015 in. to

Director of Research, Aluminum Co. of America, New Kensing-
ng Chemist, Packaging Laboratory, Aluminum Co. of America,
N. J.

is the first of a series of three articles
ituting a summation of years of re-
h by one of the leading producers of
inum foil. We predict that it will
l as the definitive reference on this
ct for a long time to come. The first
e presents data on mechanical proper-
water-vapor transmission rates, re-
vity for light and radiant heat, hygienic
teristics, resistance to corrosion and
vital information.—ED.

0.00035 in. One cubic inch of aluminum weighs about 0.0975 lb., so that one pound of aluminum foil of 0.0005 in. thickness has a covering area of 20,500 sq. in. Thinner gauges will, of course, have proportionately larger covering areas and thicker gauges smaller covering areas. Aluminum foil is rolled in widths up to about 36 in.

The reduction of sheet aluminum to foil gauges is accomplished by cold rolling and this cold working of the metal increases both strength and hardness. This, however, is accomplished with a loss of ductility and for most applications aluminum foil is annealed to put it in the soft condition. The tensile strength of annealed aluminum foil 0.001 in. thick is about 8.5 lbs. per inch of width. The annealed foil is dead-folding, which is an advantage in many packaging operations.

With constantly increasing interest in the storage of products at low temperatures, it is important to know that aluminum foil does not become brittle at low temperatures. In fact, recent measurements show that aluminum increases in strength and ductility as the temperature is lowered, even down to minus 320 deg. F.

The tearing strength of the thin gauges of aluminum foil is relatively low; however, by bonding aluminum foil to other materials, such as plastic films, paper and paperboard, a laminated product can be produced which has good strength and resistance to tear.

Water-vapor transmission of foil

An outstanding development of modern packaging practices is the control of the gas and moisture contained within a package. Usually this means control of the moisture content and the desired condition may vary over a wide range, depending on the material being packaged. In the case of tobacco and various food products, for example, the aim may be to maintain the moisture content within some preferred range. In the

PASS in a series of breakdowns in ing mills by means of which coiled m sheet is converted into form of foil.

steel products, such as ball bearings, cutlery, nim may be to maintain an atmosphere of very nidity to prevent rusting. This practice has yond the control of moisture content and now packaging in controlled atmospheres contain- on dioxide, nitrogen, etc.

ermeability of packaging materials to gases has, ently, become an important consideration and lized techniques for the measurement of gas bility are available. Aluminum, the metal, is ous to gases and this characteristic offers an nt advantage to the package designer. It must nized, however, that not all gauges of aluminum ve zero water-vapor transmission. In thick- below about 0.0015 in., foil will contain minute s. In the very thin gauges of foil, such as in., these pinholes will be of sufficiently frequent to permit an appreciable rate of moisture diffusion. However, as the foil thickness increases, the number of pinholes in any given area decreases and the size of pinhole also decreases. These pinholes seem to be an inevitable result of rolling metal to such a thin gauge; the best of rolling practices seem able only to control their size and number.

An idea of their effect upon water-vapor transmission is given by the data in Table I, which presents characteristic WVT values for foil of four different gauges. In making this test, 100 sheets (12 in. square) of each gauge of foil were taken and every tenth sheet tested for WVT. In the case, however, of the 1-mil foil, only eight of the 100 sheets showed pinholes in the test; in the case of 0.0007-in. foil, only 15 of the 100 sheets showed pinholes. In the two heavier gauges, only three pieces of the 0.001-in. foil and eight of the 0.0007-in. foil, respectively, had pinholes in the center area, where their effect on WVT could be measured. The data of Table I clearly illustrate the fact that there is considerable variation in the WVT of different test pieces of the same gauge aluminum foil. This is to be expected, of course, since any pinholes present are uniform neither in size nor in distribution. The averages, however, clearly indicate the trend toward lower per-

TABLE I—WATER-VAPOR TRANSMISSION OF ALUMINUM FOIL

Thickness of foil (in.)	*WVT (gm. H_2O per 100 sq. in. per 24 hrs. with air at 100°F. and 100% R. H.)*	*Thickness of foil (in.)*	*WVT (gm. H_2O per 100 sq. in. per 24 hrs. with air at 100°F. and 100% R. H.)*
0.00035	0.62	0.0007	0.07*
	0.11		0.08
	0.20		0.06
	0.23		0.05
	0.15		0.04
	0.69		0.08
	0.29		0.01
	0.34		0.04
	0.18		
	0.07		
	Average 0.29		
0.0005	0.08	0.001	0.02*
	0.05		0.03
	0.06		0.02
	0.12		
	0.15		
	0.09		
	0.13		
	0.31		
	0.17		
	0.04		
	Average 0.12		

Gauge of foil (in.)	*Number of 12 in. square sheets with pinholes*	*Number of sheets with no pinholes*
0.00035	100	None
0.0005	100	None
0.0007	15	85
0.001	8	92

* WVT values not averaged because majority of the 100 sheets examined had zero permeability.

...as the thickness of the foil is increased. The ...st area for the permeability measurements ...Table I and elsewhere in this paper was ap... ...y 10 sq. in.

...thod employed in measuring the permeability ...aterials to water vapor is essentially that de... ...viously in this journal (1)[1]. A glass test dish, ... calcium chloride desiccant, is closed by the ...rane which is wax-sealed at the edges. The ...after weighing, is supported in a chamber filled ...of the required temperature and humidity; ...maintained in positive circulation with a fan. ...asured period, the water-vapor transmission ...ned by weighing.

...a foil laminates

... has been made of the practice of bonding ... foil to other materials to produce laminates ...esired combination of characteristics for con... ...l wraps. These materials are usually paper ...board of wide variety and plastic films of ... kinds. In producing laminates with very ...bility, it is important that good adhesion be ... the foil. For this reason, the adhesive se... ...ld be adapted to the materials to be lami...

...e laminate is made with paper or paperboard, ...spersed adhesive such as sodium silicate, ca... ... latex or an emulsified resin composition may ...ed. Adhesives of the hot-melt type have ...ound particularly useful for this application; ...hesives comprise amorphous waxes, used ...dified with resins. Asphaltic adhesives are ... for some laminates.

...ating plastic films with aluminum foil, it is ... important that the adhesive adequately ...il and plastic. Consideration must also be ... the fact that the foil is nonadsorptive and ...e to solvent. This means that the adhe... ... be selected for the specific plastic-foil com... ... be laminated. For example, nitrocellulose... ...ves find particular application in laminating ...and other cellulosic films, whereas vinyl... ...ives have been found quite satisfactory for ... certain other types of plastic films. Ad... ...loyed with plastic films are generally of the ...ic type, applied from solution or dispersion.

...foil laminates

...hanisms by which water vapor penetrates ...tic films are quite different. In the case of ...il, water vapor penetrates by diffusion, but ...h openings such as pinholes. In the case ...lms, water vapor penetrates through the ...of the film by solution in the plastic and dif... ... one side to the other. The WVT rate is ...by the composition of the film and its thick... ...se of the difference in the method of pene... ...*binations* of aluminum foil and plastic sheet... ing offer very effective barriers to water-vapor and gas transfer.

If the foil is on the side of high humidity, water-vapor penetration is limited to the area of the pinholes. If the other side of the foil is covered with plastic sheeting and the adhesion between foil and plastic is complete, then the only areas of the plastic exposed to gas transfer are those areas outlined by the pinholes. For example, the measurements referred to on 0.00035-in. foil showed a total pinhole area of approximately 0.00004 sq. in. in 100 sq. in. of foil. Thus an extremely small area of plastic is exposed to water vapor and the moisture-excluding efficiency of the laminate is very high.

There are several problems involved in securing complete lamination of foil to plastic, but even though the plastic does not adhere to the foil at every point, a very effective combination can be secured. In Table II are given data showing the water-vapor transfer of foil laminated with two different types of plastic. These are commercial materials and examination showed that adhesion was generally good, though not complete. For comparison with these values another series of tests was run showing the permeability of the same foil and plastic simply laid one over the other without a laminating adhesive between. In this latter series of tests, any water vapor penetrating the foil could diffuse between foil and plastic and have the whole test area of the plastic available for water-vapor diffusion. Ten test pieces were run in each series to show the agreement between replicate samples. These data show that while good adhesion between foil and plastic is necessary for the most efficient barrier, water-vapor transfer is quite limited even when the foil and plastic are not laminated but form two barriers "in series," so to speak. As would be expected, these tests show that the

SKILLED OPERATORS and precision equipment are required to maintain uniform foil thicknesses. Here a strip of heavier-gauge aluminum foil is undergoing another breakdown pass.

mplete the degree of adhesion between the foil stic, the less important is the permeability of stic film.

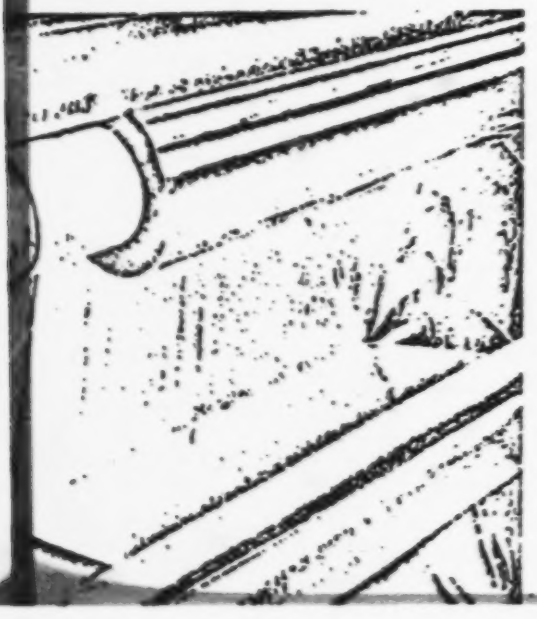
ented papers, as a rule, offer very little resistance re-vapor passage. As a result, combining paper uminum foil, particularly when it is attached by es and not an over-all adhesive, results in very

E II—EFFECT OF ADHESION BETWEEN FOIL HEETING ON PERMEABILITY OF LAMINATES

	Permeability (gm. H_2O per 100 sq. in. per 24 hrs. at 100°F. and 100% R. H.)	
Description of material	Laminated with all-over adhesive	Foil laid on plastic film—no adhesive
um foil (0.00035 in.) in nation with moisture- cellophane sheeting	0.019	0.136
	0.019	0.117
	0.011	0.058
	0.012	0.083
	0.013	0.107
	0.019	0.110
	0.020	0.100
	0.021	0.011
	0.014	0.010
	0.021	0.013
	0.017	0.081
m foil (0.00035 in.) in nating with acetate ng	0.001	0.254
	0.012	0.019
	0.021	0.015
	0.037	0.153
	0.018	0.050
	0.005	0.005
	0.015	0.200
	0.029	0.203
	0.029	0.413
	0.012	0.183
	0.018	0.150

Permeability—foil, 0.2; cellophane, 0.45; acetate, 42.0.

ROLLING can be used with foil in its gauges. Two layers of aluminum foil ed simultaneously through the rollers.



little change in the permeability of the foil. In the case of one particular lot of 0.00045-in. foil which was laminated to 35-lb. bond paper by widely spaced glue lines, the permeability of the composite product was only 15% less than that of the foil alone. That the reduction in permeability was not greater is not surprising since the paper alone, under standard tests, had a WVT of 325 gm. per 100 sq. in. per 24 hrs.

The data of Table III show that with proper laminating techniques and proper selection of materials, foil-plastic laminates having WVT values as low as 0.00 can be secured. To secure a laminate of uniformly low permeability, it is desirable to use one of the heavier gauges of foil, such as foil 0.001 in. in thickness.

TABLE III—WATER-VAPOR TRANSMISSION OF ALUMINUM-FOIL LAMINATES

Material	Thickness (in.)	Permeability (gm. H_2O per 100 sq. in. per 24 hrs. at 100°F. and 100% R. H.) Flat	Creased*
Aluminum foil laminated	0.00035	0.00	...
with moistureproof cello-	0.0009	0.01	0.03
phane		0.01	0.01
Aluminum foil laminated	0.00035	0.01	...
with cellulose acetate	0.0012	0.02	0.07
Aluminum foil laminated	0.00035	0.01	0.01
with rubber hydrochloride	0.0008	0.01	...
Aluminum foil laminated	0.00035	0.01	0.02
with vinyl polymer	0.0012	0.02	0.01
Aluminum foil laminated	0.00035	0.00	0.04
with wax to 30# glassine			
Aluminum foil 28-0	0.00035	0.07	0.42
Aluminum foil laminated	0.001	0.00	0.00
with moistureproof cello-	0.0009		
phane			
Aluminum foil laminated	0.001	0.00	0.00
with vinyl polymer	0.0012		
Aluminum foil laminated	0.001	0.00	0.02
with wax to 25# glassine			
Aluminum foil 28-0	0.001	0.00	0.40

NOTE: Each value in this table is the average of measurements on two or three test pieces. In some cases, two or more lots of laminates were tested.
* These test pieces were creased with four equidistant parallel folds and then with four more folds at right angles to the first; there were thus 16 crease intersections on the face of the test pieces.

Permeability of foil laminates to CO_2

Because of the interest in the use of carbon dioxide as an inert atmosphere in packaging, a series of measurements has been made on the permeability of two aluminum-foil laminates to this gas; these data are presented in Table IV. For comparison with the data on the laminates, permeability figures are presented for the plastic films alone. The evidence is quite convincing that although the plastic films alone show an appreciable permeability, the foil laminate is quite impervious to penetration by either carbon dioxide or water vapor. These data supplement the information presented in Table III.

Reflectivity of aluminum foil

A clean aluminum surface of high purity will exhibit a reflectivity for white light of approximately 90%. Commercial aluminum foil (Table V) may develop a

vity as high as 88%. There is a tendency for the r, more highly burnished foils to exhibit the reflectivities. In the case of embossed foils, the vity generally runs about 80 to 86%, depend- the particular foil and pattern employed. These rements show the consistently high reflectivity mercial aluminum foil.

IV—PERMEABILITY TO CARBON DIOXIDE ATER VAPOR OF ALUMINUM FOIL LAMI- NATED TO FILMS AND OF FILMS ALONE

Material	Permeability (cm. per 100 sq. in. per 24 hrs.*) CO_2†	$CO_2 + H_2O$	H_2O
m foil (0.00035 in.) ated to moisture- relhplate	0.001	0.001	0.000
m foil (0.00035 in.) ted to vinyl poly-	0.001	0.005	0.001
ne alone	0.030	0.193	0.197
lymer alone	1.78	4.18	2.72

ed values are the average of concordant measurements on four dif- s pieces at a temperature of 77 to 81 deg. F. ability to carbon dioxide measured at 760 mm. pressure difference; side in next column was saturated with water vapor.

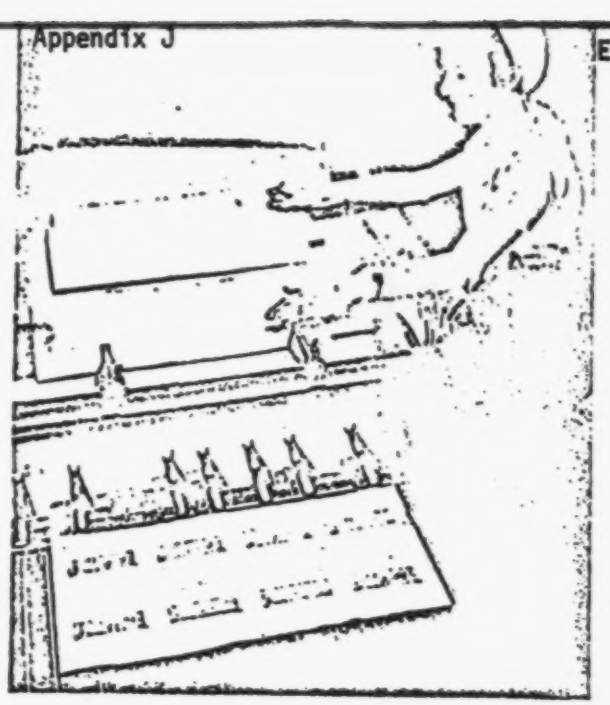
inum foil in the thinner gauges may be produced k-rolling, that is, two sheets may be passed h the rolls together. The surfaces in contact e rolls will be burnished, but the two faces of the ich are in contact with each other have a some- duller surface and one which is more diffusing in ter. While embossing may not seriously reduce tal reflectivity, it does reduce the specular re- n from the surface and correspondingly increases fuse reflection. For many applications, this in- in diffuse reflectivity is a desirable one from the oint of appearance.

V—REFLECTIVITY OF ALUMINUM FOIL FOR LIGHT
(Light from tungsten-filament lamp)

Description of foil	Total reflectivity (per cent)
minum foil—0.0005 in.	87
minum foil—0.001 in.	88
minum foil—0.002 in.	82.5
minum foil - 0.005 in.	82
l foil - 0.00045 in.- bright	86.5
l foil—0.00045 in. - medium	81
l foil 0.00045 in.—dull	80.5

high reflectivity of aluminum foil may be com- lly important because of the bright metallic nce which it contributes. The high reflectivity so be of advantage under some circumstances in izing the temperature rise in a package when d to the heating effects of sunlight or other ra- nergy.

reflectivity will be reduced by coating with syn- resin or laminating with plastic films. The t of the reduction will vary, depending on the characteristics of the material employed. Cer- tics, such as the methacrylate resins and cellu-



PRINTING on foil can be done by any of the commercial processes. Here operator feeds embossed, paper-backed foil to flat-bed press.

lose acetobutyrate, are quite transparent to light and effect a minimum reduction in reflectivity.

Aluminum foil, of course, is opaque to light.

For reflecting thermal radiation such as from a hot stove or radiator, aluminum foils have even greater efficiency. For long wave length (infra-red radiation) of this type, the reflectivity of aluminum foil may be as high as 97%. Correspondingly, its emissivity or radiating power for radiation of this same wave length will be 3%. For thermal radiation of this type, the reflectivity (and emissivity) is substantially changed by any nonmetallic coating such as resin or plastic film of appreciable thickness.

Hygienic aspects of aluminum in packaging

The fact that aluminum does not produce any toxic effects makes it an entirely safe packaging medium. This fact has been established not only by scientifically controlled experimental investigations, but also by long experience, particularly with aluminum cooking utensils. Carefully controlled tests have proved that contact with aluminum, in contrast to a number of other metals, does not accelerate the loss of vitamins in cooking. The loss of vitamin C during pasteurization of milk in an aluminum container was no greater than when pasteurized in contact with glass. The loss due to heating under these conditions was about 30%, while pasteurization of milk in copper completely destroyed vitamin C (2). This is only one reason why aluminum foil caps have proved so satisfactory in the bottling of milk.

Another advantage of aluminum foil is the sterile character of the surface which results from [illegible] at a temperature of about (*Continued on page*

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Tin restrictions issued

The long-awaited tin-conservation order made its appearance on Jan. 30, in much milder form than had originally been expected. In general, it merely restricts can manufacturers to the use of no more tin in 1948 than was used by them in 1947. The announcement of the Department of Commerce order stated that it was designed to save 2,750 tons of tin for the nation's dwindling strategic stock-pile.

The order forbids entirely the use of tinplate cans for coffee, forcing that product into non-tinned metal, glass or paper. Motor oil is allowed no one-quart tinplate cans, although terneplate may be used. Animal foods are restricted to no more than 75% of the tinplate coating used in 1947 or 1941, whichever is larger, and are allowed no tinplate can ends. Pigmented oil paints may use no cans with a tin coating heavier than 0.25 lb. per base box, but terneplate may be substituted.

The use of cans for beer is in effect frozen at the 1947 level by a provision that beer may use no more tinplate than it used in 1947.

The order will become effective Feb. 29 only if Congress extends government controls on tin beyond that date, but this action is generally expected.

Aluminum foil

(*Continued from page 147*) 700 deg. F. Aluminum foil is also odorless, tasteless and does not absorb odors from the surrounding atmosphere.

Resistance of aluminum to corrosion

The resistance of aluminum to attack by various materials is an important consideration in some applications of aluminum foil and other aluminum products used for packaging. There are certain conditions met with in packaging which may have a significant effect and which sometimes make necessary a special appraisal of a new packaging problem. Such factors as temperature of storage of the package, probable time of storage, thickness of the foil, etc., must be given careful consideration. Aluminum foil is unaffected by sunlight, is noncombustible and, being nonsorptive, does not exhibit dimensional change with change in the humidity of the atmosphere. While intermittent contact with water generally has little action on aluminum, moist or hygroscopic products packed in thin foil may cause some reaction, particularly if the product contains salt, or salt and some organic acid, as in the case of cheese. The action may be quite severe and require a protective coating on the metal. Solutions of heavy metal salts, such as those of copper, nickel, tin, etc., have a corrosive action on aluminum. Soaps and detergents are generally sufficiently alkaline so that they attack the natural protective oxide film on aluminum and it becomes necessary to pack them in coated foil. Oils and greases, as a rule, have little or no action. How-

over, the only safe rule is to make a packaging test in the case of any new type of product.

Aluminum foil may be coated with lacquers and synthetic-resin coatings of various kinds. It is common practice, for example, to apply colored lacquers to foil for decorative purposes. These lacquers are usually made with a nitrocellulose base and are the quick-drying type, so that the foil may be coiled immediately after lacquering. Usually the lacquer is colored with a dye. These coatings, generally thin, offer little protection.

Where the foil must be heat sealing, a synthetic-resin coating of the thermoplastic type is employed. The resin should, of course, be selected to give adequate sealing within a permissible temperature range. For some purposes, foil is given a heat-sealing coating on one side and laminated on the other side to a thermoplastic sheeting. Foil can also be coated with thermoplastic synthetic-resin coatings which are not only heat sealing, but offer substantial protection against mildly corrosive products and environments.

By the use of quick-drying "metal" inks, foil can be printed on directly for the purpose of labeling and decoration. Printing can also be done over lacquer coatings or plastic films laminated to foil. The nonsorptive character of the foil requires the use of inks specially developed for this type of application.

The second article in this series next month will show how aluminum foil and foil laminates can be employed efficiently in bags, cartons and other type containers.

References

1. "Measuring Permeability to Carbon Dioxide and Water Vapor," J. D. Edwards and D. B. Strahm, Morgan Packaging 19 (Oct., 1943).
2. "Bibliography on the Hygienic Aspects of Aluminum and Aluminum Utensils," G. D. Beal, et al., Bulletin No. 3, Mellon Institute of Industrial Research, Pittsburgh, 1933.

Cosmetic foresight

(*Continued from page 109*) volved the adoption of the basic package design to price lists, letterheads, counter and window displays, so that starting in April, 1917, the new integrated program was ready to show to the trade. In introducing the line, HQZ replaced all existing inventory of old merchandise with an equal value for the new. "This was extremely well received by dealers," said Mr. Conwell, "still lacerated and bruised by the kicking around they got during the war.

"It was a Herculean job, but very soon the effect began to show on the ledgers. June, July, August, September and October figures surpassed corresponding months in 1915 and 1916 by from 10 to 45%," he stated. "Distribution is expanding, profits are growing. Definitely, HQZ has reversed its trend by taking drastic action when drastic action was needed."

CREDITS: *Designer, Norman Slewer, San Francisco. Labels, Mercury Press, San Francisco. Closures, manufactured by Armstrong Cork Co., Lancaster, Ohio, and supplied by I. F. Schnier Co., Inc., San Francisco. Bottles, Owens-Illinois Glass Co., San Francisco. Displays, Kobrand Co., San Francisco.*

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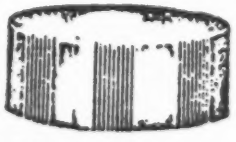

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Foreword

The fabrication of VINYLITE resins into new forms regularly creates new problems in the cementing of these resins to themselves, and to a variety of other materials. In recent years, a number of efficient solution adhesives have been developed, and these are now available for commercial use. These cements will answer the need for a satisfactory bonding material in a great many applications, although their use will not solve all bonding problems.

The bonding problem is complicated by the fact that there are a number of types of VINYLITE resins available. These may be formulated in different ways, and such formulations can be used to bond an extremely wide variety of materials, such as aluminum, glass, bronze, wood, cement, and many others.

This booklet includes, first of all, a summary of the generally used methods of bonding VINYLITE resin compounds. Detailed suggestions for standard combinations follow. This information can be used as a basis for study and experimentation whenever unusual bonding problems are encountered. If the reader is faced with a bonding problem not covered by this information, or which cannot be solved with commercial VINYLITE resin adhesives, the Plastics Division of Carbide and Carbon Chemicals Corporation will be pleased to offer suggestions.

The Bonding of VINYLITE Resins

The very properties which make VINYLITE resins so valuable to industry, namely, chemical inertness, toughness, and insolubility, make it difficult to bond these resin compounds to themselves and to other materials. Chemical inertness, associated with high intermolecular forces, is an indication of the incompatibility of the vinyl resins with other materials. Two incompatible materials are held together by comparatively weak forces which are, in general, insufficient to bond an incompatible resin to the plastic material. This sharply limits the number of materials which may serve as a base for an adhesive for use with VINYLITE resins. Only a few incompatible resins have been used successfully to modify the properties of other resins which are compatible with the vinyl resin.

The low solubility of the vinyl resins mitigates against solvent welding, accomplished so readily with the more soluble resins, such as the cellulose esters. Despite this fact, there are laminating thinners which can be used in solvent welding plasticized sheeting to itself.

In a brief outline of the subject of bonding VINYLITE resins it is patently impossible to cover all of the variety of conditions which might be encountered. In fact, nearly every cementing job is unique. Inasmuch as the success or failure of the bonding is often of major importance in the application of VINYLITE resins, it is well to study the particulars involved so that these general facts can be used in solving individual bonding problems.

Bonding Methods

There are four general methods of bonding VINYLITE plastics. These are: 1. the use of one of the solvents which has a solvating effect on the resin; 2. the use of a cement prepared by dissolving a resin in a solvent; 3. the use of certain of the pressure-sensitive adhesives; and 4. the use of heat-sealing operations.

Detailed suggestions for bonding vinyl resins will be included in the later discussion, but, first, it would be well to consider the bonding methods in general.

1. SOLVENT BONDING

There are several good solvents generally referred to as laminating thinners, which will soften adjacent plastic surfaces to such an extent that they will adhere. These solvents, in effect, serve as a cold welding method of joining two plastic surfaces. The bond formed by this method has considerable strength immediately after application. The ultimate strength of the bond is reached as soon as the solvent evaporates. The strength of the joint, when these bonds are properly prepared, is practically as high as that of the original plastic. Careful attention to the details of application is necessary to insure the success of this bonding method.

2. SOLUTION ADHESIVES

A bond can be formed by the use of a resin compound dissolved in a solvent. In use, the solution forms a bond with each of the surfaces being joined, and thus the success of the method depends upon the holding power of the solution itself. These adhesives set very slowly, and have little strength immediately after application. The strength of the bond increases slowly as the solvent evaporates.

3. PRESSURE-SENSITIVE ADHESIVES

Pressure-sensitive adhesives, typified by rubber cements are used in a great many industrial operations because of their high initial strength, and the wide latitude allowable in bonding time. This type of cement depends upon the tackiness of a solvent-free film to adhere the surfaces. Tackiness is usually obtained through the use of plasticizers or soft resins in the compound. The initial bond strength is generally the highest strength that will be achieved unless the adhesive film is vulcanized.

4. HEAT-SEALING

The fourth method is one which has gained prominence as a production method comparatively recently. It is the joining of the plastic surfaces by pressing together areas softened by heat, or by a combination of heat and solvent. This is, in effect, welding the surfaces together. The strength of the bond immediately after sealing is dependent upon the temperature of the surfaces. As soon as the sheets have cooled to room temperature, the strength of the bond will be practically as high as that of the original plastic. Automatic sealing machines which utilize heat to achieve the bond have been developed by several companies for their own use. Commercial machines are still being perfected. These machines develop temperatures ranging from 200 to 500 deg. F. They operate on much the same principal as a seam welder, or a production sewing machine. The temperature, the speed of bonding, and the pressure applied are adjusted to the thickness of the plastic and to the compound used.

Adhesive Materials

Some of the materials used in these methods of bonding VINYLITE plastics are discussed in the following:

Solvents: The ketones are the most powerful solvents that have been discovered for vinyl chloride-acetate resins. The cyclic ketones form solutions with the highest solids content, but they evaporate rather slowly, and, in general, are used only for grade VYNW resins. Mixtures of ketones and aromatic hydrocarbons have a faster solvent action than do the ketones alone. Propylene oxide is also extremely valuable in speeding the solution of VINYLITE resins, and it increases the bite of the solvents into the plastic surfaces, particularly those based upon grade VYNW resin. Adequate ventilation should be employed where solvents are used.

Resins: The vinyl chloride-acetate resins, Grades VYNW, VYNS, VYHH, and VMCH, can all be used in adhesives. Resin VYNW requires the strongest solvents, forms solutions of low solids content and longest drying time, but yields films of the greatest flexibility, fatigue life, and resistance to change with temperature. Because of its better solubility characteristics, resin VYNS is widely used as an adhesive for VYNW sheeting, but adhesives made with this resin are inferior to VYNW adhesives in fatigue life and temperature range. Resin VYHH is used only when a reduction in adhesive strength can be tolerated and where adhesives must have a high solids content, and so a resin of greater solubility than VYNS is required. These adhesives cannot be used where fatigue life and flexing are the most important considerations. Resin VMCH has much the same properties as the VYHH resin, but it also has the property of releasing solvents more rapidly. Moreover, it is the only vinyl chloride-acetate resin which adheres to nonporous surfaces without baking. For this reason,

has been widely used in adhesive formulations. The vinyl chloride-acetate resins used in adhesives do not develop a high degree of tackiness either in solution or in a film wet with solvent or plasticizer. This limitation can be overcome to some extent by incorporating in the vinyl resin adhesive certain resins such as the acrylic and methacrylic ester resins, rosin, rosin esters and coumorone resins. These resins are compatible with vinyl chloride-acetate resins and adhere to VINYLITE resin surfaces. For this reason they are used in other types of adhesives to improve their adhesion to VINYLITE plastics. A list of such compatible resins is given in Table 1. These soft adhesive resins are seldom used alone as adhesives for flexible VINYLITE sheeting because most of the plasticizers used in the sheeting soften these resins to a greater extent than they do the VINYLITE resin. As a result a coating of one of these resins in contact with VINYLITE plasticized sheet will soften progressively as long as contact is maintained. This softening is minimized when the resin adhesive contains the less soluble VINYLITE resins.

Table I

Resins Compatible with VINYLITE Resin VYNS

Acrylic and Methacrylic Types:	Supplier, See Key on Page 16
ACRYLOID A-10	18
ACRYLOID B-7	18
ACRYLOID B-72	18
ACRYLOID B-75	18
ACRYLOID F-10	18
Ethyl Methacrylate Polymer	8
n-Propyl Methacrylate Polymer	8
Methyl Methacrylate Polymer	8
n-Butyl Methacrylate Polymer	8
Isobutyl Methacrylate Polymer	8

Acrylic and methacrylic resins increase the wet strength of adhesives. Butyl methacrylate resins lower softening point of VINYLITE resin adhesives.

Synthetic Rubber:	
HYCAR OR-15	13
HYCAR OR-25	13

HYCAR plasticizes and softens VINYLITE resin. It requires 20 to 30 minutes' milling on a differential rubber mill before dissolving.

Gum and Rosin Derivatives:	
Ester Gum	2
Wood Rosin	11
Hydrogenated Rosin and Derivatives	11

Gum and rosin derivatives impart tackiness to adhesives, but the wet strength is not usually very great. On drying, the adhesive may tend to be brittle.

Sulfonamid-Formaldehyde Resins	Suppliers, See Key on Page 16
SANTOLITE Resins MS and MHP	14
Phenolics:	
BAKELITE RESIN BR-254	4
BR-2987	4
XR-3180	4
XR-3360	4
XR-4357	4
DUREZ 550	9
Coumarone-Indene Resins:	
CUMAR P-10	1
CUMAR P-25	1
Alkyds:	
DURAPLEX A-25	18
DURAPLEX C-45	18
GLYPTAL 2451	10
GLYPTAL 2454	10
REZYL 110	2
PETREX 7, 21, and 22	11
Chlorinated Resins:	
Chlorinated diphenyls	7, 14
Chlorinated paraffins	4, 11, 12
Chlorinated rubber (slightly incompatible)	11
Natural Resins:	
Accroides	—
Elemi	—

Pressure-Sensitive Adhesives: Adhesives of this type which are based on natural rubber do not adhere well to VINYLITE plastics. However, the Buna N types of synthetic rubber, particularly Hycar OR, are compatible, and yield excellent adhesives for many purposes. Details of the formulation of these adhesives can be obtained from the sales literature of Hycar Chemical Company. Even better adhesion to VINYLITE plastics, and higher strength, can be obtained by blending vinyl chloride-acetate resins with the synthetic rubber. Tackiness is also promoted by the use of Cumar resins, or by the addition of plasticizers. The film should be vulcanized after the coated surfaces have been united in order to eliminate the tackiness and to achieve maximum strength of the bond.

Fast acting accelerators, such as Butyl 8, are required for low temperature vulcanization with most Hycar base adhesives, while Altax, Captax, and similar types of accelerators yield good results where the bonded surfaces can be heated. Vulcanization of these solution adhesives will take place slowly even at room temperature. Therefore, such self-vulcanizing adhesives should be formulated in two portions, and these two portions mixed together shortly before using. The vulcanization accelerator, and a portion of the elastomer are put into solution in one part of this cement. The major portion of the elastomer, and all other compounding ingredients, including specifically the sulfur, and zinc oxide, are dispersed in the second part of the cement.

Hycar OR, and VINYLITE VYNS resin can be used together to formulate a pressure-sensitive adhesive which does not require an accelerator. Such adhesives can also be classified under the second method of bonding noted in the foregoing, as tackiness is secured through solvent retention, and solvent evaporation is all that is necessary to obtain a bond.

Plasticized Sheet and Sheeting

BONDING TO PLASTICIZED SHEETING

A rapid and strong bond for joining plasticized sheeting to itself is obtained in many instances through the use of solvents. No heat, and very little pressure, is required to effect this bond. A balanced and active solvent mixture found extremely useful is XT-5033 shown in Table II. It is necessary to add a word of caution concerning the effect of the sheet composition on the bond obtained, since radically different results are obtained with different compositions. For example, the presence of certain waxes in the sheeting often prevents the establishment of strong bonds.

There are a few instances where the use of solution cements in preference to solvents alone has proved advantageous. In these instances, solutions of VYNS or VYNW in XT-5033 have been recommended. For example, when the bond formed between two sheets must sustain a small force immediately after the surfaces are joined, cement XL-5174, Table III, a solution of resin VYNW in XT-5033, has been used successfully. This adhesive is also valuable when a short time must elapse between the application of the adhesive, and establishment of the bond. A similar adhesive, XL-5173, a solution of VYNS with higher solids content, has been used when cloth or other decorative materials are to be laminated between VINYLITE resin surfaces.

In still another type of application, a solution of VYNW in XT-5033 at 12 to 15 per cent solids is used. Since a solution of this concentration forms a gel on standing at room temperature, it must be prepared and used warm (that is, 95 to 115 deg. F.). Such a hot solution applied to plasticized sheeting can be used to form a strong, immediate bond, such as required when sheeting is to be bonded under tension.

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Table II
Laminating Thinners

	XT-5015	XT-5020	XT-5021	XT-5033	Supplier, See Key Page 16
	Part by Weight				
Kronisol	5	2.5	2.5		16
Methyl Acetate (82 per cent)	58				5
Ethyl Acetate (85 per cent)	10				5
Butyl Acetate	10				5
Methyl Ethyl Ketone		63		40	5
Dioxane		20			5
Isophorone		2.5	2.5		5
Methylene Dichloride			50		8
Ethylene Dichloride			43		5
Cyclohexanone				40	1
Propylene Oxide				20	5
Trioluoil	15				3
Acetic Acid	2	2.0	2.0		—
Methanol		10			5
	100	100	100	100	

Formulation Notes:

The acetic acid is added as a wetting agent.

The plasticizer (Kronisol) improves the bond in the faster acting thinners, especially where moisture might be condensed on the sheet due to evaporation of the solvent. It is possible that the plasticizer also minimizes embrittlement, but, in general, it should be eliminated from thinners containing high boiling-point solvents.

Propylene oxide is one of the speediest penetrants known for vinyl chloride-acetate resins, and this solvent improves the "bite" into the material when used up to 20 to 25 per cent of the thinner. It should not be used with acetic acid. If propylene oxide evaporates too rapidly, acetone may be used as a substitute. Since propylene oxide is extremely volatile, boiling at 95 deg. F., care should be taken in storage of the adhesives which include this solvent in order to prevent its evaporation.

The chlorinated hydrocarbons are excellent solvents for VINYLITE resin, and well suited for use in laminating thinners. The toxic hazards involved in the use of these solvents mitigate against their use except where excellent ventilation is provided. These solvents present less of a fire hazard than do other types of solvents, but the odors of the chemicals are objectionable to many people.

Cyclohexanone and isophorone are extremely high-boiling solvents which contribute slow drying and long tack life to adhesives. Used alone, they are very slow penetrants, and are, therefore, preferably diluted with low-boiling solvents. The other ketones, acetone, methyl ethyl ketone, methyl isobutyl ketone, are excellent solvents.

The esters are weak solvents for VYNS resin, but they appear to be released somewhat faster and more completely than ketones. The commercial esters are usually mixtures of the pure ester and the corresponding alcohol. The presence of the alcohol aids in preventing the excessive softening of the VINYLITE resin sheet. The fact that ethyl acetate, butyl acetate, and amyl acetate are important components of fingernail lacquers makes their odors familiar, and therefore more acceptable to women workers. For this reason, when it is necessary to have a solvent stronger than XT-5015, it is often desirable to modify this thinner by replacing all or part of the Trioluoil with a ketone of appropriate evaporation rate retaining the esters.

Sheeting has also been bonded to itself successfully through the use of pressure-sensitive Vyvar adhesives discussed on page 8, and detailed in Table IV.

Heat-sealing methods similar to those noted on page 6 are also used successfully in joining plasticized sheeting. Faster and easier sealing at lower platen temperatures may be accomplished if the surfaces are first wet with a solvent such as XT-5033. Many unique products such as desalinating kits, bags for treating burns with liquid, gun covers and others, are fabricated in this manner.

BONDING TO METAL AND CERAMIC SURFACES

The bonding of plasticized sheeting to metal and similar non-porous surfaces can be accomplished by several systems. In this field, commercial adhesives* are of special value. The bonding systems often require the application of a VINYLITE resin primer to the surface to which the plasticized sheeting is to be cemented. A VMCH resin solution, such as XL-5252, Table VI, or a pigmented variation of this cement, may be applied to the metal surface in a light coat.

Table III
Solution Adhesives

	XL-5129	XL-5151	XL-5170	XL-5171	XL-5173	XL-5174	XL-5181	XL-5221	Supplier, See Key Page 16
	Parts by Weight								
Resin VYNS	10		12		20			2	5
Resin VYNW						10			5
Poly-n-butyl-methacrylate	10	32	12	20					8
Rosin			6						11
Chlorinated rubber 1000 cp							25.0		11
Plasticizer E-60							12.5		12
Methyl ethyl ketone	80		70	70	32	36	62.5	96	5
Cyclohexanone					32	36			1
Propylene Oxide					16	18			5
Toluol		34							3
Solvesso No. 2		34							19
Petrex No. 21				10					11
Acetic Acid								2	
	100	100	100	100	100	100	100.0	100	

*A list of manufacturers of available commercial adhesives will be sent on request.

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Table IV

HYCAR Base Adhesives

	XL-5199	XL-5238	XL-5256	Suppliers, See Key, Page 16
	Parts by Weight			
Resin VMCH	10.0		10.0	5
Hycar OR-15	10.0	13.0	10.0	13
Cumar P-25		4.3		1
Dioctyl Phthalate		4.3		5
Nitroethane		12.9	7.5	6
Methyl Ethyl Ketone	80.0	65.0	16.1	5
Ethyl Acetate			16.0	5
Methyl Isobutyl Ketone			20.0	17
Toluene			20.0	—
Sulfur		0.3	0.2	—
Captax		0.2	0.2	20
	100.0	100.0	100.0	

Air drying for 24 hours is desirable, but a short bree dry at 200 to 225 deg. F. is equally satisfac- ory. A VYHH, or VYNS resin primer can be sed, but these solutions require baking at 350 to 75 deg. F., and are somewhat limited in their usefulness since they may lose their adhesion to the metal in the presence of an excess of active Vinylite resin solvent. Formula XE-90, Table VI, is typical of a baking primer, but other Vinylite resin coatings are equally applicable.

Table V

Emulsion Adhesive

	XL-5213	Supplier, See Key, Page 16
	Parts by Weight	
125c.p. Chlorinated Rubber	25.4	11
Chlorinated Paraffin (60 per cent of chlorine)	12.7	11, 12
Toluene	41.3	—
Sodium Oleate	1.0	2
Water	19.6	—
	100.0	

Note: Add water and soap to the chlorinated rubber – chlorinated paraffin solution with rapid agitation.

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Table VI

Adhesive Primers

	XL-5123*	XL-5220	XL-5252	XE-90	Supplier, See Key, Page 16
	Parts by Weight				
Resin XYNC	10				5
Resin VMCH		4.75	28		5
Resin VYNS		4.75			5
Resin VYHH				14.80	5
Santicizer B-16			6		14
Kronisol				2.72	16
Methanol	30				5
Dioxane	60				5
Methyl Ethyl Ketone		24.80	20		5
Methyl Isobutyl Ketone		31.00	20	29.20	5
Isophorone		3.30			5
Propylene Oxide			1		5
Methyl Amyl Ketone				7.30	5
Toluene		28.10	25	29.20	–
Xylene		3.30		7.30	–
Blue Lead				9.48	–
	100	100.00	100	100.00	

*Prolonged breathing of the solvent vapors should be especially avoided.

Where a wide range of bonding times are desired, a pressure-sensitive adhesive of the Hycar type, such as XL-5238, Table IV, is recommended. Where a shorter tack life is permissible, the VMCH type adhesive, XL-5252, has proved useful. This is applied to both surfaces and dried to a satisfactory tack, after which the surfaces are faced and held together under pressure. For quicker bonding, the surfaces are coated with XL-5252, permitted to dry, then the solvent is reactivated just before bonding.

In some instances, heat, or heat and pressure, can be used in the bonding process. An adhesive, such as XL-5129, Table III, applied to the sheet is advisable since this cement has a lower bonding temperature than the resin. The coated sheeting can be pressed on to a metal surface, previously coated with XE-90, Table VI, after the metal has been heated to 325 to 375 deg. F. Little pressure is required to achieve the bond. When this process can be completed quickly, sheeting under some tension can be bonded successfully.

Sometimes, where stress will not be imposed on the bond, a temporary or pressure-sensitive adhesive, such as XL-5171, Table III, or Goodyear Cement No. AF 12C, will give adequate bond strength to non-porous surfaces.

BONDING TO LEATHER

Several types of adhesives have been used for bonding plasticized sheeting to leather. Resin

VMCH, or VYNS adhesives adhere readily to the leather surface, and will unite the plasticized sheeting to leather if the surfaces are faced while the adhesive is still tacky. Somewhat better tack is obtained if softening resins and plasticizers are added to the adhesive. Typical examples of such formulations are XL-5129, and XL-5170, Table III. Adhesives containing mixtures of VINYLITE resins and Hycar OR also are valuable in bonding VINYLITE resins to leather. This type can be used under a wide variety of conditions. The cement, XL-5199, Table IV, is an example of a simple air-dry type, while XL-5256 is a typical vulcanizing type.

BONDING TO WOOD

A variety of adhesives is available for use on wood, including commercial types, and the choice depends largely on the conditions required for the bonding and the surface of the wood to be joined. The strongest bonds have been established with two-coat systems since the adhesives which bond best to plasticized sheeting are not particularly well suited for use on wood. There are several good wood primers available. These may be based on resin XYNC, VINYLSEAL adhesive MA 28-18 or pyroxylin-vinyl acetate. The primed wood is then bonded to the sheeting with a solution containing one of the acrylate resins, such as Acryloid A-10, or B-7, or a chlorinated rubber adhesive such as formula XL-5181, Table III. When cement XL-5181, or XL-5180, are used as single coat adhesives, somewhat weaker bonds are obtained. Cement XL-5180 has the advantage of quicker tack.

These adhesives for wood were developed to provide a tacky surface suitable for bonding under a wide variety of conditions. Where it is necessary to bond sheeting under tension, and into sharp depressions, it is often advisable to use some type of heated tool to heat the sheet and to bond through plastic flow.

BONDING TO CONCRETE, WALLBOARD, AND SIMILAR MATERIALS

Concrete, or a similar surface, should be primed with a VYHH, or VMCH lacquer, before bonding. The sheeting can then be cemented to this surface while the lacquer is still tacky. A preferable method is to bond the plasticized sheeting to the dried primer through the use of a VYNS-Hycar adhesive. When the concrete or plaster surface is quite rough, the use of a heavy-filled primer is advisable.

BONDING TO CLOTH

The choice of an adhesive for bonding plasticized sheeting to cloth depends largely upon the fabrication method preferred. One of the most satisfactory methods involves the priming of the cloth with a VYNW, or a VYNS solution, drying, and then bonding the cloth and sheeting under heat and pressure. Typical cloth primers would be:

	A	B	Suppliers, See Key, Page 16
	Parts by Weight		
Resin VYNS	18		5
Resin VMCH	2		5
Resin VYNW		14	5
FLEXOL DOP	18	5.5	5
Methyl ethyl ketone	25	40.5	5
Cyclohexanone		40	1
Hexone	23		5
SOLVESSO No. 1	14		19
	100	100	

Penetration of the coating into the cloth will improve adhesion, but it will also lower the flexibility of the combination. Therefore, some variation in solvent and plasticizer contents of these coatings will have to be made to fit individual requirements and coating conditions. The VYNW coating would be preferred where the coating must withstand extremes of temperature.

The plasticized sheeting can also be bonded to the cloth through the use of heat and pressure, or a solution adhesive can be used. Priming VINYLITE resin sheet surface with XL-5129,

Table III, lowers the temperature requirement for bonding, but, likewise, it lowers the high temperature bond strength.

In other instances, rather strong bonds can be obtained if a heavy solution of a VINYLITE resin adhesive is applied to the cloth, and the sheeting bonded to this while the adhesive is still wet with solvent. Heating at 180 to 250 deg. F. to remove the solvent is desirable in order to obtain a strong bond.

BONDING TO RUBBER E49

Only in a few exceptional cases have adequate bonds of VINYLITE resins to soft rubber been obtained. In these instances, a Goodyear cement No. AF 12C, was used. It is probable that in some cases a multiple coat system, using a rubber compatible synthetic as a primer, with increasing quantities of Buna N rubber in the subsequent coats, will bond VINYLITE plastic to rubber.

Bonding Thin Films

Thin films of VINYLITE plasticized resin can be bonded to themselves and to other materials simply and quickly through the use of heat and moderate pressure. In some instances, when adhering films to paper or textiles, a strong bond can be achieved by pressing the film against the surface to be bonded with a hot laundry iron or photographic hot press. Heat-sealing of the films to themselves can be accomplished with similar equipment designed for continuous production processes. In some instances, it is advantageous to achieve initial adhesion by first softening a portion of the area with solvent, and facing the sheets in position.

Bonding Molded and Extruded Products

The success of the bonding of molded and extruded products to sheeting, to themselves, or to other materials, will depend on the surfaces available for adhesion. The smaller the available area, the less chance there is to secure an adequate bond. Procedures to be followed are largely dependent on individual conditions. The bonding methods to be used are the same as those recommended for similar types of plasticized resins.

Bonding Coated Cloth To Coated Cloth

Cloth with a relatively thin coating of VINYLITE resin can be bonded to itself successfully through the use of various heat-sealing methods. When the cloth has a heavier coating, the use of a solution adhesive is recommended. One such adhesive which has been used successfully with cloth coated with VYNS and VYNW resins is XE-5127-1, shown in Table VII. It is suggested that this adhesive be prepared in the following manner: Mill Hycar 20 to 30 minutes; add pigments and filler; add sulfur last; mill an additional 3 to 5 minutes; soak stock in nitroethane for at least one hour; follow with mixing of the solution, and the addition of dioctyl phthalate

...l Cumar, thin the heavy paste with remaining ...lvent while agitating thoroughly; add Captax ...m freshly prepared 10 per cent methyl ethyl ...tone solution the same day adhesive is to be ...ed. If it is desirable to prepare the adhesive ...nsiderably in advance of use, it is advisable to ...ke a two-part adhesive solution with the sul...r, zinc oxide, and part of the Hycar in one ...tion, and the Captax in the second part. These ...rts are then mixed just prior to use.

In the event that the shortage of Hycar makes it impossible to formulate adhesive XE-5127-1, the solution adhesive shown with this cement in Table VII can be employed. In preparing this adhesive, the BAKELITE resin, XR-9396, is heated to 100 to 150 deg. C., and poured into cold isophorone. The solution is then stirred until it is clear and uniform. Then propylene oxide is added, and finally, the VYNS resin is stirred in. The viscosity of the finished product can be adjusted by varying the amount of propylene oxide. This adhesive has good wet strength, fair tack

Table VII

Adhesives For VINYLITE Resin Coated Cloth

	XE-5127-1	"Dewey and Almy" HYCAR Replacement*	XL-5246	Supplier, See Key, Page 16
	Parts by Weight			
...sin VYNS		7.14		5
...sin XYHL (dry)			9	5
...AKELITE Resin XR-9396		7.14		4
...AKELITE Resin XV-16530			50	4
...YCAR OR	15.2			13
...AKELITE Hydrogenerated Rosin			18	11
...UMAR P-25	4.9			1
...hiting	15.15			—
...on Oxide Black	3.6			—
...on Oxide Yellow	3.6			—
...nc Oxide	3.6			—
...ioctyl Phthalate	4.9		18	5, 16
...itroethane	18.9			6
...ethyl Ethyl Ketone	14.9			5
...hyl Acetate, 95 per cent	14.9			5
...ophorone		14.29		5
...opylene Oxide		71.43		5
...cetone			5	5
...lfur	0.35			—
	100.00	100.00	100	

*...ake ... before using.

lite, adheres well to both cloth and vinyl chloride-acetate resin coatings, and gives an adequately strong bond. If cloth coated with vinyl butyral resin is to be bonded, cement XL-5246, Table VII, is recommended. Again, the presence of certain waxes or lubricants in the coating compound often prevents the establishment of a strong bond.

Bonding Coated Paper To Coated Paper

In practically all cases, coated paper is bonded to itself through the use of heat and moderate pressure, although laminating thinners may be used with equal success. Conditions of the operation are dependent upon the type of paper used, and formulation of the coating.

Variations May Be Necessary

The procedures discussed in the foregoing, and the formulations given, are believed to be adequate for practically all bonding of VINYLITE plastics to themselves, and to other materials. A number of excellent solution adhesives are available on the industrial market, and a list of such adhesive manufacturers will be sent on request. Nevertheless, the extreme range of materials to be bonded, and the infinite variety of conditions to be overcome makes it highly probable that the procedures and formulations will have to be modified in some instances to meet specific conditions. This is especially true in regard to the solvents used in the formulations. Such modification is an individual problem, and can be solved only through experimentation. It is recommended that the bonding procedures be tested thoroughly to be certain of their adequacy in production operations before entering into large-scale use.

SUPPLIERS OF CHEMICALS AND RESINS

1. Allied Chemical & Dye Corporation, Barrett Division, 61 Broadway, New York, N. Y.
2. American Cyanamid Company, 30 Rockefeller Plaza, New York, N. Y.
3. Anderson-Prichard Oil Corporation, Oklahoma City, Oklahoma.
4. Bakelite Corporation, 30 East 42nd Street, New York, N. Y.
5. Carbide and Carbon Chemicals Corporation, 30 East 42nd Street, New York, N. Y.
6. Commercial Solvents Corporation, 17 East 42nd Street, New York, N. Y.
7. Dow Chemical Company, 919 Jefferson Avenue, Midland, Michigan.
8. E. I. DuPont DeNemours & Company, Inc., Wilmington, Delaware.
9. Durez Plastics & Chemicals, Inc., 1911 Walck Road, North Tonawanda, N. Y.
10. General Electric Company, 111 Plastics Avenue, Pittsfield, Massachusetts.
11. Hercules Powder Company, Inc., 908 Market Street, Wilmington, Delaware.
12. Hooker Electrochemical Company, 1940 Ward Street, Niagara Falls, N. Y.
13. Hycar Chemical Company, Akron, Ohio.
14. Monsanto Chemical Company, 1700 So. Second Street, St. Louis, Missouri.
15. The Neville Company, 1938 Neville Island, Pittsburgh, Pa.
16. Ohio-Apex, Inc., Nitro, West Virginia.
17. Pittsburgh Plate Glass Company, 2222 Grant Building, Pittsburgh, Pennsylvania.
18. The Resinous Products & Chemical Company, Inc., 222 W. Washington Square, Philadelphia, Pennsylvania.
19. Standard Oil Company of New Jersey, 26 Broadway, New York, N. Y.
20. R. T. Vanderbilt Company, Inc., 943 Gene Street, East Norwalk, Connecticut.

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Aug. 3, 1954 G. F. NADEAU ET AL 2,685,511

METAL REINFORCED CELLULOSE ESTER PHOTOLITHOGRAPHIC PRINTING PLATES

Filed May 3, 1952

Fig. 1

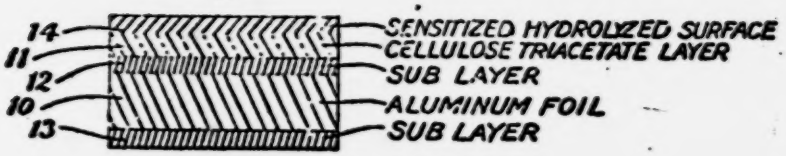


Fig. 2

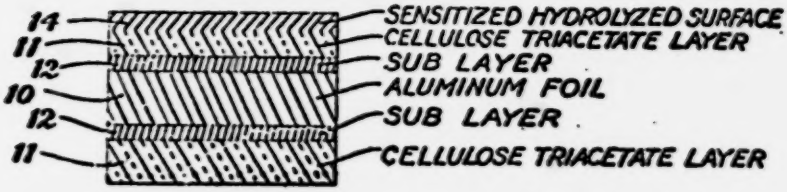


Fig. 3

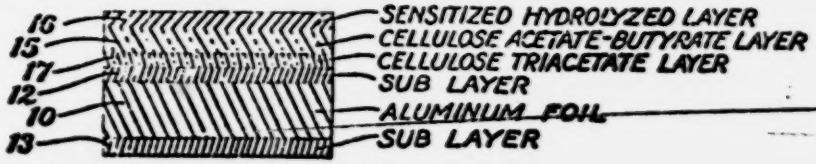
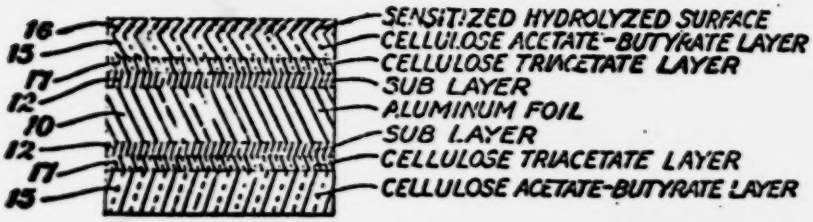


Fig. 4



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Patented Aug. 3, 1954

2,685,511

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UNITED STATES PATENT OFFICE

2,685,511

METAL REINFORCED CELLULOSE ESTER PHOTOLITHOGRAPHIC PRINTING PLATES

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Application May 3, 1952, Serial No. 285,934

12 Claims. (Cl. 95—8)

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This invention relates to the preparation of an improved light-sensitive photographic element and more particularly to such element protected against halation and free from dimensional and chemical instability and especially designed for use in making lithographic printing plates.

This application is a continuation-in-part of our copending application Serial No. 173,378, filed July 12, 1950, now Patent No. 2,635,962 of April 21, 1953.

Printing plates of the photolithographic type are well known having been prepared previously, for example, from metal plates carrying light-sensitive colloid layers and from cellulose ester plates carrying similar light-sensitive stratum or layer. R. S. Colt, in United States Patent 2,448,851, dated September 7, 1948, describes a method for preparing cellulose ester type printing plates according to which a surface hydrolyzed cellulose ester sheet is sensitized with a bichromate such as potassium bichromate, and after exposure under a design, the exposed area is removed with aqueous solutions of chlorites or hypochlorites such as, for example, sodium hypochlorite, thereby producing ink-receptive areas in the region of the exposure and ink-repellant areas, when moistened, in the region of the unexposed areas. It is highly desirable in a process of the above kind to include an antihalation layer and, following the usual practice in the art, it might appear that the antihalation layer coated on the rear surface of the sensitive plate would provide adequate protection from halation effects. However, it has been found that when such elements are subjected to alkaline hydrolysis by immersion methods to produce a stratum of hydrolyzed cellulose ester on the surface of the plate, the dye later tends to be removed in the process leaving the residual dye in uneven and mottled condition, as well as contaminating the hydrolysis bath with dyestuff. Another disadvantage of such elements is that while satisfactory as a printing plate for short runs, on continued running they tend to stretch and pull out from clamps of the type used on many small offset printing presses. Accordingly, such elements have been found to lack dimensional and chemical stability for precision registration on long continued runs.

While reinforcing materials such as thin metal foils have been proposed heretofore for reinforcing various cellulose ester photographic elements, all attempts to produce a highly satisfactory type of surface hydrolyzed and sensitized cellulose ester printing plate provided with a thin metal foil reinforcement have failed for one reason or another. For example, when thin metal foil is

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used as the reinforcing material, the usual binding pastes or cements tend to break down and allow the cellulose ester coat or sheet to pull away from the metal foil at the edges of the composite plate, especially when the composite element or plate is subjected to the action of aqueous caustic solutions in the step of forming the surface hydrolyzed layer or surface on the cellulose ester coating or sheet. Subsequent treatment by various processing solutions and by prolonged use of the finished printing plate in contact with printing inks caused a similar distortion or peeling at the edges of the plate. Where the reinforcing metal foil is a desirable metal such as zinc or aluminum, the aqueous caustic hydrolyzing solution vigorously attacks and corrodes such metal foils. Protective coatings or backings commonly employed to protect metal surfaces, when applied to the exposed back surface of the metal foil of the above type of composite plate have been found impractical to use or ineffective in that the bonding of the metal to the cellulose ester or to the protective coating or backing does not hold as firmly as desired, or in that the protective coating or backing is etched or dissolved away under the hydrolyzing action of the caustic solution.

We have now found that excellent light-sensitive photographic elements designed for preparing lithographic printing plates, and especially elements which are protected against halation effects and intimately bonded to reinforcing metal foil, and which have none of the aforementioned disadvantages of dimensional instability and adverse susceptibility to processing solutions, can be prepared as described hereinafter.

It is, accordingly, an object of our invention to provide light-sensitive elements having dimensional and chemical stability, and more particularly such elements protected against halation, for use in making lithographic printing plates. A further object is to provide lithographic printing plates having dimensional and chemical stability. Another object is to provide novel processes for preparing such photographic elements and printing plates. Other objects will become apparent hereinafter.

In the accompanying illustrative drawings Figs. 1–4, Fig. 1 is an enlarged, diagrammatic cross-sectional view of a light-sensitive photographic element comprising a thin aluminum foil having an outer layer on one side of cellulose triacetate.

Fig. 2 is similar to Fig. 1 but denotes an aluminum foil having outer layers on both sides of cellulose triacetate.

Fig. 3 is similar to Fig. 1 but differs therefrom

in that the aluminum foil has an outer layer on one side of cellulose acetate-butyrate.

Fig. 4 is similar to Fig. 3, but differs therefrom in that the aluminum foil has outer layers on both sides of cellulose acetate-butyrate.

In accordance with our invention, we prepare our new light-sensitive photographic elements of the surface hydrolyzed and sensitized cellulose organic acid ester type in a number of modifications, wherein the reinforcing material is a metal foil of from 0.002–0.005-inch thickness, depending on what type and thickness of element is desired. One form of the invention comprises an element having an overall thickness of approximately 0.006-inch and is prepared by bonding a coated layer from a solution or dope of a cellulose organic acid ester preferably containing an antihalation dye incorporated therein to a metal foil such as zinc, aluminum, etc., preferably aluminum foil, by means of an interlayer or sublayer coated on the foil comprising a resinous, thermoplastic material, the other side of the foil being protected against the hydrolyzing and processing solutions by a similar layer of a resinous, thermoplastic material coated thereon, curing the coated foil and subjecting it to a hydrolyzing bath, followed by sensitization of the resulting hydrolyzed outer surface of the cellulose organic ester layer with a suitable sensitizing agent. Another form of the invention having an overall thickness of approximately 0.005-inch and particularly free from curl is prepared as above, but the cellulose organic acid ester in solution or dope form is applied as a coating to both sides of the subbed metal foil and at least one of the resulting outer surfaces is hydrolyzed and sensitized. Mixtures of one or more cellulose organic esters can be used. A particularly valuable element is one wherein the hydrolyzed and sensitized outside layer is a cellulose acetate-butyrate. When this kind of layer is subjected to hydrolysis, sensitized, exposed under a pattern and developed, the small halftone dots obtained are much stronger and show greater resistance to removal by swabbing action with aqueous caustic during processing than is the case with elements wherein the outer layer is some other cellulose organic acid ester such as, for example, cellulose triacetate. However, the cellulose acetate-butyrate shows relatively poor adhesion to the subbing layer. Consequently, to obtain a good quality element having an outer surface of cellulose acetate-butyrate, the metal foil is first subbed as before, then coated with a solution of a different cellulose organic acid ester to give a relatively thin layer of the ester, preferably cellulose triacetate, and then overcoated with a relatively thicker layer of a solution of cellulose acetate-butyrate preferably containing the antihalation dye. In this kind of composite element a layer of cellulose acetate-butyrate can be used for the hydrolyzed and sensitized surface or stratum and the other side of the foil can be a layer of any of the other cellulose organic acid esters, for example, a layer of cellulose triacetate. The subbing, coating and hydrolysis processes lend themselves readily to continuous form of operations.

Suitable cellulose organic acid esters which we employ for preparing the above-described products of our invention are substantially fully esterified esters including cellulose acetate having the maximum resistance to moisture and containing about 43.5% by weight of acetyl groups, and other esters of equivalent acyl content such as cellulose propionate, cellulose butyrate, cellulose acetate-propionate, cellulose acetate-butyrate, etc. The preferred outer surface is cellulose acetate-butyrate wherein the proportions of acetyl to butyryl can vary over a wide range, for example, 6% Bu. and 38% acetyl to 20% Bu. and 29% acetyl but preferably we use cellulose acetate-butyrates containing 17.5% Bu. and 30% acetyl. As previously mentioned the cellulose organic esters are applied in solution or dope form in one or more volatile solvents such as methylene chloride, ethylene dichloride, acetone, mixtures of these with up to about 20% by weight of one or more lower alcohols such as ethanol, methanol, etc. The solutions or dopes intended for coating an outer surface of approximately 0.001-inch thickness are adjusted to a concentration sufficient for this purpose which depends upon the characteristics of the particular cellulose ester, but generally a concentration of from 6–12% has been found efficacious. The antihalation dye is incorporated in such solutions. Where cellulose acetate-butyrate is used as the outer layer to be hydrolyzed and sensitized, the intermediate cellulose triacetate solution functions as a cement between the subbed metal foil and the layer of cellulose acetate-butyrate, and is made up in similar solvents in concentrations of about from 0.5–2% by weight of cellulose triacetate. The thickness of this intermediate layer in dried condition does not ordinarily exceed 0.0001-inch, although much thicker layers can be used, if desired.

In the hydrolysis step, the outer cellulose ester surface of the composite reinforced foil is hydrolyzed on the surface to the predetermined depth always leaving a stratum of unhydrolyzed material. This is accomplished by simply immersing the cellulose ester coated metal foil for a few minutes in an aqueous alcoholic solution of a caustic alkali (e. g. sodium hydroxide, potassium hydroxide, lithium hydroxide, etc.), followed by washing the hydrolyzed product with water, neutralizing residual alkali with weak acid solution such as 1–5% aqueous acetic acid. In the case where cellulose ester coatings are made to both sides of the metal foil, if desired, only one side need be hydrolyzed by simply applying the hydrolyzing solution to this side as by swabbing action, and the like. The concentration of the hydrolyzing solution can be varied to some extent, depending on the time of exposure, the temperature of the bath and the degree of hydrolysis desired. A suitable solution is 5% sodium hydroxide in equal parts of ethyl alcohol and water, which gives good hydrolyzing results at 70° C. in about 3–5 minutes exposure. By operating at 60° F., the time required is somewhat longer, whereas at 100° F. the required time is considerably shorter and more critical.

The subbing solutions which give sublayers having satisfactory adhesion to metal foils, particularly to aluminum foil, and to layers of cellulose organic acid esters coated from the aforementioned solutions or dopes, particularly to layers of cellulose triacetate coated from such solutions, are the subbing solutions prepared with interpolymers of various mixtures of vinyl chloride and vinyl acetate which contain a small proportion of free carboxylic acid groups. A suitable subbing solution consists of 6% by weight of a ternary interpolymer containing approximately 86% by weight of vinyl chloride groups, 13% by weight of vinyl acetate groups and 1% by weight of α,β-unsaturated dicarboxylic acid

groups such as maleic or fumaric acid groups, 45% by weight of butyl acetate and 45% by weight of methylene chloride. In place of methylene chloride, other solvents in admixture with each other or with methylene chloride can be employed such as acetone, 1,4-dioxane, ethylene dichloride, etc. The concentration of the interpolymer in solution can be varied from about 1–10%, but preferably an approximately 6% solution of the above interpolymer or of generally similar interpolymers can be employed.

The antihalation dye employed in the process of our invention is selected from those which absorb in the blue and ultraviolet regions of the spectrum, and which are compatible with the cellulose organic acid ester solutions used for providing the coated layer of cellulose ester over the subbed metal foil. The preferred dye (or mixture of dyes) is used in a concentration of about 0.5–3%, although considerable variation is possible.

Suitable sensitizers include compounds which like bichromate (e. g. ammonium bichromate, sodium bichromate, potassium bichromate, etc.) will quickly oxidize hydrolyzed cellulose organic acid esters, in the presence of blue or ultraviolet light transmitted by a design such as a line or half-tone negative, to an alkali-soluble state, and include other sensitizing compounds such as ferric ammonium oxalate, which can be used in conjunction with a ferricyanide (e. g. potassium ferricyanide, etc.) and which is reducible to ferrous salt images in the presence of light, but which does not oxidize cellulose in the presence of light, so that is necessary in this case to use alkaline oxidizing solutions such as hydrogen peroxide in dilute aqueous alkali metal hydroxide (e. g. sodium hydroxide, potassium hydroxide, etc.) to effect removal of the hydrolyzed cellulose ester in the exposed area. For a detailed description of suitable sensitizers and subsequent development of the relief images, reference can be had to Kenyon and Unruh, U. S. Patent 2,548,537, dated April 10, 1951.

The following examples and cross-sectional drawings will serve to illustrate further our new halation-free and dimensionally and chemically stable, light-sensitive, photographic elements, and the manner for preparing the same.

Example 1

A light-sensitive photographic element designed for preparing a lithographic printing plate of approximately 0.006-inch thickness was prepared by first subbing an aluminum foil of 0.0045-inch thickness on both sides with a solution consisting of 6% of an interpolymeric resin containing 86% by weight of vinyl chloride groups, 13% by weight of vinyl acetate groups and 1% by weight of dibasic acid groups such as maleic or fumaric acid groups, in methylene chloride, drying the sublayer, and then coating a layer of cellulose acetate solution over one of the subbed surfaces of the aluminum foil in such manner that there results an aluminum foil having on one side a firmly bonded layer of cellulose acetate of approximately 0.0015-inch thickness. The solution employed for coating the aluminum foil consisted by weight of 8% of cellulose triacetate, 50% of methylene chloride, 7% of isopropyl alcohol and 5% of ethylene chloride. An antihalation dye which absorbs light in the blue region of the spectrum such as Cesar [illegible] in J. B. Dickey, U. S. Patent 2,264,303, dated December 2, 1941, particularly p-nitrobenzene-azo-3-hydroxyethyl-o-chloroaniline, was incorporated in the cellulose acetate coating solution or dope in an amount equivalent to 1% based on the weight of the solution. After curing the subbed and coated foil, it was surface hydrolyzed on the side having the outer cellulose triacetate coating by passing the coated foil through 5% sodium hydroxide dissolved in equal parts of ethyl alcohol and water, the hydrolyzing time being approximately 3 minutes at a bath temperature of 70° F. The hydrolyzed coated foil was then passed through an acid stop bath consisting of 2% acetic acid in water, washed with fresh water and dried. By this treatment there was obtained a hydrolyzed stratum of cellulose triacetate of a thickness on the order of one micron. By varying the hydrolytic conditions, the thickness of the hydrolyzed stratum can be varied to about half thickness or increased to twice or even three times the above figure. The hydrolyzed composite foil produced as described remained perfectly flat, showed no tendency to peel, the antihalation dye in the unaffected part of the cellulose triacetate layer remained of even shades, and the sandwiched-in-aluminum foil was entirely unaffected by the hydrolysis treatment. In the case where the subbing solution is applied only to the side of the foil which is to be coated with the cellulose triacetate solution, then prior to the hydrolysis step the other face of the foil must be coated with a thin coating of resinous protective material such as the subbing solution to protect the metal from the etching action of the caustic hydrolyzing bath.

The hydrolyzed composite foil was then sensitized by treating the hydrolyzed surface with an aqueous solution of ammonium bichromate under non-actinic light conditions, and the sensitized composite foil dried. The light-sensitive photographic element thus obtained was then exposed under a suitable design such as a line or half-tone negative to actinic light, and developed to a relief image by lightly swabbing the exposed surface with a 2% aqueous caustic soda solution. The brown image which had formed on exposure soon disappeared and the hydrolyzed cellulose triacetate was gradually removed from the exposed area. Following neutralization of the excess alkali with 2% aqueous acetic acid solution, it was found that the exposed and developed areas readily received greasy printing inks, whereas the areas containing unexposed hydrolyzed cellulose triacetate, when moistened, repelled such inks. The dried product thus obtained was free from dimensional distortions and weaknesses and gave excellent results as a printing plate over an extended period of operation in a press. Other of the mentioned sensitizers can be used in the above example in place of the ammonium bichromate.

The light-sensitive photographic element prepared as described in the above example is shown in cross-section in Fig. 1, wherein the cellulose triacetate layer 11 having an outer sensitized hydrolyzed stratum 14 and an antihalation dye incorporated therein, is firmly bonded as shown to a thin aluminum foil 10 by means of a thin layer 12 of subbing compound which acts as an adhesive, and wherein the other side of the foil is protected with a layer 13 of the subbing compound or some other equivalent resin material which is unaffected by the caustic hydrolyzing bath.

Example 2

A light-sensitive photographic element designed

for preparing a lithographic printing plate of approximately 0.006-inch thickness was prepared by first subbing an aluminum foil of 0.003-inch thickness on both sides with a solution consisting of 6% of an interpolymeric resin containing 86% by weight of vinyl chloride, 13% by weight of vinyl acetate and 1% by weight of dibasic acid groups such as maleic or fumaric acid groups, in methylene chloride, drying the subbed foil and then overcoating it with a cellulose triacetate solution in such manner that there resulted an aluminum foil having on each side firmly bonded thereto a layer of cellulose triacetate of approximately 0.0015-inch thickness. The coating solution consisted by weight of 8% of cellulose triacetate, 80% of methylene chloride, 7% of isopropyl alcohol and 5% of ethylene chloride. An antihalation dye which absorbed light in the blue region of the spectrum such as described by J. B. Dickey, U. S. Patent 2,264,303, dated December 2, 1941, particularly p-nitrobenzene-azo-p-hydroxyethyl-o-chloroaniline, was incorporated in the cellulose triacetate coating solution in an amount equivalent to 1% based on the weight of the dope. After curing the double coated aluminum foil, it was subjected to hydrolysis by swabbing one of the coated surfaces with aqueous alcoholic caustic solution, followed by sensitization with ammonium bichromate, etc. following the procedure described in Example 1. The sensitized photographic element so produced was exposed through a suitable design to actinic light and the relief image developed. Excellent results were obtained with this printing plate on long extended operation in a printing press.

The light-sensitive photographic element prepared as described in the above Example 2 is shown in cross-section in Fig. 2, wherein cellulose triacetate layer 11 having an antihalation dye incorporated therein and having an outer hydrolyzed sensitized stratum 14, is firmly bonded as shown to a thin aluminum foil 13 by means of a thin layer 12 of subbing compound which acts as an adhesive, and wherein the other side of the foil is similarly bonded by means of the subbing compound 12 to a layer of cellulose triacetate 11 which may or may not contain an antihalation dye.

Example 3

A light-sensitive photographic element designed for preparing a lithographic printing plate of approximately 0.006-inch thickness was prepared by first subbing an aluminum foil of 0.0045-inch thickness both sides with a solution consisting of 6% of an interpolymeric resin containing 86% by weight of vinyl chloride groups, 13% by weight of vinyl acetate groups and 1% by weight of dibasic acid groups such as maleic or fumaric acid groups, in methylene chloride, drying the sub layer, then coating a thin layer of 1.5% solution of cellulose triacetate in methylene chloride over one of the subbed surfaces of the aluminum foil, drying the coated foil, and then overcoating the layer of cellulose triacetate with an 8% solution of cellulose acetate-butyrate (containing 30% acetyl groups and 17.5% butyryl groups) in a 90:10 mixture of ethylene dichloride and methyl alcohol, and containing 0.15% of triphenyl phosphate as a plasticizer, 0.75% of an orange dye, p-nitrobenzeneazo-p-hydroxyethyl-o-chloroaniline and 1.0% of a yellow dye such as o-nitro-p-chlorobenzeneazo-5,5-dimethyl-1,3-cyclohexadione, based on the weight of cellulose acetate-butyrate, in such manner that the dried layer of cellulose acetate-butyrate had approximately 0.001-inch thickness. After curing the double coated foil, the outer cellulose acetate-butyrate surface was hydrolyzed by passing the composite foil through 5% sodium hydroxide dissolved in equal parts of ethyl alcohol and water, the hydrolyzing time being approximately 3 minutes at a bath temperature of 70° F. The hydrolyzed foil was then passed through an acid stop bath consisting of 2% aqueous acetic acid, washed with fresh water and dried. By this treatment there was obtained a hydrolyzed stratum of cellulose acetate-butyrate on the order of one micron. By varying the hydrolytic conditions, the thickness of the hydrolyzed stratum can be varied to about half thickness or increased to twice or even three times the above figure. The hydrolyzed composite foil produced as described remained perfectly flat, showed no tendency to peel, the antihalation dyes in the unaffected part of the cellulose acetate-butyrate layer remained of even shades, and the sandwiched-in-aluminum foil was entirely unaffected by the hydrolysis treatment. In the case where the subbing solution is applied only to the side of the foil which is to be coated with the cellulose organic acid ester, then prior to the hydrolysis step the other face of the foil must be coated with a thin coating of resinous protective material such as the subbing solution to protect the metal from being etched by the caustic hydrolyzing bath.

The hydrolyzed composite foil was then sensitized by treating the hydrolyzed surface with an aqueous solution of ammonium bichromate under non-actinic light conditions and the sensitized composite foil dried. The light-sensitive photographic element thus obtained was then exposed under a suitable design such as a line or half-tone negative to actinic light, and developed to a relief image by lightly swabbing the exposed surface with a 2% aqueous caustic soda solution. The brown image which had formed on exposure soon disappeared and the hydrolyzed cellulose acetate-butyrate was gradually removed from the exposed area. The elevated portions of the relief image (unexposed areas) were more sharply defined and stronger than similar reliefs produced as described in Example 1. Following neutralization of the excess alkali with 2% aqueous acetic acid solution, it was found that the exposed and developed areas readily received greasy printing inks, whereas the areas containing unexposed hydrolyzed cellulose acetate-butyrate, when moistened, repelled such inks. The lithographic plate so produced was free from dimensional distortions and weaknesses even after long periods of operation, and its printing face gave superior printings and had much longer useful life period of operation than was found with similar plates having printing faces produced with other of the mentioned cellulose organic acid esters such as, for example, with cellulose triacetate printing faces.

The light-sensitive photographic element prepared as described in the above example is shown in cross-section in Fig. 3, wherein the cellulose acetate-butyrate layer 15 having an outer sensitized hydrolyzed stratum 16 and an antihalation dye incorporated therein, is firmly bonded as shown to a thin layer of cellulose triacetate 17 and this latter layer is in turn bonded firmly to a thin aluminum foil 10 by means of a thin layer 12 of subbing compound, and wherein the other side of the aluminum foil is protected with a layer 13 of

the subbing compound or some other equivalent resin material which is unaffected by the caustic hydrolyzing bath.

Example 6

A light-sensitive photographic element designed for preparing a lithographic printing plate of approximately 0.006-inch thickness was prepared by first subbing an aluminum foil of 0.003-inch thickness on both sides with a solution consisting of 6% of an interpolymeric resin containing 86% by weight of vinyl chloride, 13% by weight of vinyl acetate and 1% by weight of dibasic acid groups such as maleic or fumaric acid groups, in methylene chloride, drying the subbed foil and then coating a thin layer of 1.5% solution of cellulose triacetate in methylene chloride over both of the subbed surfaces, drying the coated foil, and then overcoating this layer of cellulose triacetate on each side of the foil with an 8% solution of cellulose acetate-butyrate (containing 30% acetyl groups and 17.5% butyryl groups) in a 90:10 mixture of ethylene dichloride and methyl alcohol, and containing 15% of triphenyl phosphate, 0.75% of an orange dye, p-nitrobenzeneazo-β-hydroxyethyl-o-chloroaniline, and 1.0% of a yellow dye, o-nitro-p-chlorobenzeneazo-5,5-dimethyl-1,3-cyclohexadione, based on the weight of the cellulose acetate-butyrate, in such manner that each of the dried layers of cellulose acetate-butyrate had a thickness of approximately 0.001-inch. After curing, one of these surfaces was then hydrolyzed, sensitized, exposed, developed and dried as described in Example 3. The printing plate so produced had similarly good properties as that described in Example 3.

The light-sensitive photographic element prepared as described in above Example 4, is shown in cross-section in Fig. 4, wherein cellulose acetate-butyrate layer 15 having an antihalation dye incorporated therein and having an outer hydrolyzed sensitized stratum 16, is firmly bonded as shown to a thin layer of cellulose triacetate 11 and this latter layer is in turn bonded firmly to a thin aluminum foil 10 by means of a thin layer 12 of subbing compound, and wherein the other side of the aluminum foil is similarly attached by means of thin layers 12 and 17 to cellulose acetate-butyrate layer 15 which may or may not contain an antihalation dye.

By proceeding as shown in the foregoing examples, other operable light-sensitive photographic elements can be prepared, for example, by replacing the outer layers of cellulose triacetate and cellulose acetate-butyrate with layers of cellulose propionate, cellulose butyrate or cellulose acetate-propionate. For some purposes it may be desirable to hydrolyze and sensitize both outer surfaces of elements such as those of Examples 2 and 4. The elements wherein cellulose acetate-butyrate is employed as the outer layer need not have the antihalation dye incorporated in the cellulose acetate-butyrate layer, since it is also practical to incorporate such antihalation dyes in the intermediate cellulose triacetate layer. However, the antihalation dye can also be incorporated in the sub layer of any of the light-sensitive photographic elements of our invention. Although the invention has been illustrated in all of the examples with elements containing an antihalation dye in one or more layers on the light sensitive side of the element, it will be understood that elements of more limited application which contain no antihalation dye in any of the layers are also included in our invention.

The coating technique employed for preparing the light-sensitive photographic elements of the invention is according to well-established procedures for obtaining flat, smooth, bubble-free layers of the material to be coated. Generally, the solution or dope is coated at or slightly above room temperature and then cured at elevated temperatures, but substantially below the boiling point of the solvent. The actual coatings can be accomplished by immersion, by coating from a hopper with a coating knife arrangement, by extrusion or spraying methods.

What we claim is:

1. A light-sensitive photographic element comprising a metal foil and a coated layer of cellulose organic acid ester bonded together with an interlayer comprising a resinous interpolymer of vinyl chloride, vinyl acetate and an α,β-ethylenically unsaturated dicarboxylic acid adherent thereto, the said cellulose organic acid ester layer having a hydrolyzed stratum on its outer surface sensitized with an agent selected from the class consisting of oxidants for cellulose in the presence of light and light-reducible ferric salts incapable of oxidation of cellulose to the alkali-soluble state in the presence of light, and the said aluminum foil having the outer surface thereof covered with a layer of the said resinous interpolymer.

2. A light-sensitive photographic element comprising a metal foil and a coated layer of cellulose organic acid ester bonded together with an interlayer comprising a resinous interpolymer of vinyl chloride, vinyl acetate and an α,β-ethylenically unsaturated dicarboxylic acid adherent thereto, and wherein at least one of said layers on the light-sensitive side of the foil contains an antihalation dye, the said cellulose organic acid ester layer having a hydrolyzed stratum on its outer surface sensitized with an agent selected from the class consisting of oxidants for cellulose in the presence of light and light-reducible ferric salts incapable of oxidation of cellulose to the alkali-soluble state in the presence of light, and the said aluminum foil having the outer surface thereof covered with a layer of the said resinous interpolymer.

3. A light-sensitive photographic element comprising an aluminum foil and a coated layer of cellulose triacetate bonded together with an interlayer comprising a resinous interpolymer of vinyl chloride, vinyl acetate and an α,β-ethylenically unsaturated dicarboxylic acid adherent thereto, the said cellulose triacetate layer containing an antihalation dye incorporated therein and having a hydrolyzed stratum on its outer surface sensitized with an agent selected from the class consisting of oxidants for cellulose in the presence of light and light-reducible ferric salts incapable of oxidation of cellulose to the alkali-soluble state in the presence of light, and the said aluminum foil having the outer surface thereof covered with a layer of the said resinous interpolymer.

4. A light-sensitive photographic element comprising an aluminum foil and a coated layer of cellulose triacetate bonded together with an interlayer comprising a resinous interpolymer of vinyl chloride, vinyl acetate and an α,β-ethylenically unsaturated dicarboxylic acid adherent thereto, the said cellulose organic acid ester layer containing an antihalation dye incorporated therein and having a hydrolyzed stratum on its outer surface sensitized with an agent selected from the class consisting of oxidants for cellulose

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in the presence of light and light-reducible ferric salts incapable of oxidation of cellulose to the alkali-soluble state in the presence of light, and the said aluminum foil having the outer surface thereof covered with a composite layer of the said resinous interpolymer adjacent to the foil and a layer of the said cellulose triacetate adhered thereover.

5. A light-sensitive photographic element comprising an aluminum foil and a coated layer of cellulose acetate-butyrate bonded together with one interlayer adjacent to the foil comprising a resinous interpolymer of vinyl chloride, vinyl acetate and an α,β-ethylenically unsaturated dicarboxylic acid and a second interlayer comprising cellulose triacetate adjacent to the layer of cellulose acetate-butyrate, the said cellulose acetate-butyrate layer containing an antihalation dye incorporated therein and having a hydrolyzed stratum on its outer surface sensitized with an agent selected from the class consisting of oxidants for cellulose in the presence of light and light-reducible ferric salts incapable of oxidation to the alkali-soluble state in the presence of light, and the said aluminum foil having the outer surface thereof covered with a layer comprising the said resinous interpolymer.

6. A light-sensitive photographic element comprising an aluminum foil and a coated layer of cellulose acetate-butyrate bonded together with one interlayer adjacent to the foil comprising a resinous interpolymer of vinyl chloride, vinyl acetate and an α,β-ethylenically unsaturated dicarboxylic acid and a second interlayer comprising cellulose triacetate adjacent to the layer of cellulose acetate-butyrate, the said cellulose acetate-butyrate layer containing an antihalation dye incorporated therein and having a hydrolyzed stratum on its outer surface sensitized with an agent selected from the class consisting of oxidants for cellulose in the presence of light and light-reducible ferric salts incapable of oxidation to the alkali-soluble state in the presence of light, and the said aluminum foil having the outer surface thereof covered with a thin layer of the said resinous interpolymer adjacent to the foil and a layer of the said cellulose acetate-butyrate adhered thereover.

7. A method for preparing a photographic element which comprises subcoating both sides of a metal foil with a composition comprising an interpolymer of vinyl chloride, vinyl acetate and an α,β-ethylenically unsaturated dicarboxylic acid, then coating at least one side of said subcoated foil with a composition comprising cellulose organic acid ester and hydrolyzing the outer stratum of at least one of said coatings of cellulose organic acid ester.

8. A method for preparing a photographic element which comprises subcoating both sides of an aluminum foil with a composition comprising an interpolymer of vinyl chloride, vinyl acetate and an α,β-ethylenically unsaturated dicarboxylic

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acid, then coating one side of said subcoated foil with a composition comprising cellulose triacetate and an antihalation dye, and hydrolyzing an outer stratum of the said overcoating of cellulose triacetate.

9. A method for preparing a photographic element which comprises subcoating both sides of an aluminum foil with a composition comprising an interpolymer of vinyl chloride, vinyl acetate and an α,β-ethylenically unsaturated dicarboxylic acid, then coating both sides of said subcoated foil with a composition comprising cellulose triacetate and an antihalation dye, and hydrolyzing an outer stratum of at least one of said coatings of cellulose triacetate.

10. A method for preparing a photographic element which comprises subcoating both sides of an aluminum foil with a composition comprising an interpolymer of vinyl chloride, vinyl acetate and an α,β-ethylenically unsaturated dicarboxylic acid, then coating one side of said subcoated foil with a composition comprising cellulose triacetate, and then overcoating the layer of cellulose triacetate with a composition comprising cellulose acetate-butyrate and an antihalation dye, and hydrolyzing an outer stratum of the said cellulose acetate-butyrate.

11. A method for preparing a photographic element which comprises subcoating both sides of an aluminum foil with a composition comprising an interpolymer of vinyl chloride, vinyl acetate and an α,β-ethylenically unsaturated dicarboxylic acid, then coating both sides of said subcoated foil with a composition comprising cellulose triacetate, and then overcoating both the layers of cellulose triacetate with a composition comprising cellulose acetate-butyrate and an antihalation dye, and hydrolyzing an outer stratum of at least one of said layers of cellulose acetate-butyrate.

12. A method of preparing a photographic element which comprises subcoating both sides of an aluminum foil with a composition comprising an antihalation dye and an interpolymer of vinyl chloride, vinyl acetate and an α,β-ethylenically unsaturated dicarboxylic acid, then coating at least one side of the subcoated foil with a composition comprising cellulose organic acid ester and hydrolyzing the outer stratum of at least one of said coatings of cellulose organic acid ester.

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